

I. A Study of the Conductivity of Certain Electrolytes in Water, Methyl and Ethyl Alcohols, and Binary Mixtures of These Solvents. II. The Relation between Conductivity and Viscosity.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

CHARLES GEIGER CARROLL

EASTON, PA. :
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CONTENTS.

Acknowledgment.....	3
Introduction and historical review	5

I.

Experimental part	9
Apparatus	9
Solvents.....	10
Preparation of solutions.....	11
Conductivity measurements	11
Cadmium iodide	11
Sodium iodide	15
Calcium nitrate	19
Hydrochloric acid	22
Sodium acetate	24

II.

Dissociation in 50 per cent. methyl alcohol	27
Potassium iodide.....	28
Sodium iodide.....	29
Ammonium bromide	31
Ammonium iodide.....	31
Lithium nitrate.....	32
Hydrochloric acid	32
Dutoit and Aston's hypothesis.....	34
Cause of the minimum in conductivity	34
Former views.....	35
Conclusions as to cause.....	36

III.

Viscosity and conductivity	51
Historical review	51
Views as to the cause of dissociating power ..	54
Hypothesis and evidence.....	56

IV.

Summary and conclusions.....	66
Biography.....	68

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This investigation was undertaken at the suggestion of Professor H. C. Jones and was carried out under his supervision.

I. A Study of the Conductivity of Certain Electrolytes in Water, Methyl and Ethyl Alcohols, and Binary Mixtures of these Solvents. II. The Relation between Conductivity and Viscosity.

INTRODUCTION AND HISTORICAL REVIEW.

Prior to the proposal of the theory of electrolytic dissociation by Arrhenius, a number of investigations were carried out in which the conductivities of non-aqueous solutions were studied. Since the proposal of the theory there has been a still greater number of similar investigations. These are particularly interesting in the light of certain hypotheses as to the cause of the dissociating power of a solvent. To these hypotheses, and to some of the work in non-aqueous solvents, reference will be made subsequently.

Much less has been done on conductivities in mixtures of solvents. A brief review of what has been accomplished in this field is given.

Lenz¹ measured the conductivities of various salts, potassium iodide, bromide, and chloride, sodium chloride, etc., in mixtures of methyl and ethyl alcohols and water.

He found that in certain cases the relative resistances can be obtained from the equation

$$r = 100 (1 + bv),$$

where 100 is taken as the resistance of an aqueous solution of the same per cent, v is the volume per cent of alcohol, and b ,

¹ Mem. de. l'Acad. de St. Petersbourg, 7, 30 (1881).

a constant. The formula holds best for the mixtures of methyl alcohol and water.

Stephan¹ studied the conductivities of dilute solutions of sodium, potassium, and lithium chlorides, and sodium and potassium iodides in mixtures of ethyl alcohol and water. His investigation will be given a more detailed consideration in a later part of this dissertation.

Kablukoff² determined the conductivity of hydrochloric acid in ethyl alcohol containing varying amounts of water.

Arrhenius³ investigated the changes in the conductivity of aqueous solutions resulting from the addition to them, of small quantities (less than 10 per cent by volume) of non-electrolytes, such as methyl or ethyl alcohols, cane-sugar, acetone, etc. He found that the changes could be expressed by the empirical formula,

$$l = l_0 \left(1 + \frac{a}{x} \right)^2,$$

where l is the conductivity in water, l_0 that in the mixture, x the volume per cent of added non-electrolyte, and a a constant peculiar to each non-electrolyte. Where two non-electrolytes were added a similar empirical formula was found to hold. The coefficient a differs not only for different non-electrolytes and different electrolytes, but varies also with concentration, and is greatest when dissociation is least.

Arrhenius concludes that the amount of dissociation is not appreciably changed by addition of small quantities of non-electrolytes. This follows from the fact that the alteration in conductivity is independent of the concentration. Further, he found that the velocity of inversion of cane-sugar is not appreciably influenced by addition of small amounts of non-electrolytes.

¹ Wied. Ann., 17, 673 (1882).

² Ztschr. phys. Chem., 4, 432 (1889).

³ *Ibid.*, 9, 487 (1892).

Holland¹ worked in the same field as did Arrhenius. His results will be referred to again. Strindberg² repeated and confirmed some of Arrhenius' (*loc. cit.*) work.

Wakeman³ measured the conductivities of various electrolytes, sodium and potassium chlorides, hydrochloric acid, and numerous organic acids, in mixtures of ethyl alcohol and water (containing 10, 20, 30, 40, and 50 per cent of alcohol).

For the cases studied, the equation

$$\frac{\Delta}{p(100-p)} = \text{const.}$$

was found to hold, where Δ is the difference between the conductivity of the electrolyte in water and in the mixture respectively, and p is the per cent of alcohol by volume.

Schall⁴ determined the conductivity of picric acid in aqueous alcohol.

Zelinsky and Krapiw⁵ studied the conductivities of sodium and ammonium iodides and bromides in water, methyl alcohol, and a mixture of the two containing 50 per cent of water by weight, for dilutions from $v = 16$ to $v = 1024$.

Here a striking phenomenon was observed. The conductivities in the 50 per cent mixture were found to be decidedly less than the corresponding conductivities in the pure solvents. This minimum is best seen when the results are plotted as curves, with the conductivities as ordinates and the composition of the mixture as abscissae.

Cohen⁶ observed the minimum in the case of potassium iodide. He made a study of the conductivity of potassium iodide in mixtures of ethyl alcohol and water (containing 20, 40, 60, 80, and 99 per cent alcohol). The dilutions ranged from $v = 64$ to $v = 2048$. The minimum manifested itself in the 80 per cent mixture beyond the concentration $v = 512$.

¹ Wied. Ann., **50**, 261 (1893).

² Ztschr. phys. Chem., **14**, 161 (1894).

³ *Ibid.*, **11**, 49 (1893).

⁴ *Ibid.*, **14**, 701 (1894).

⁵ *Ibid.*, **21**, 35 (1896).

⁶ *Ibid.*, **25**, 31 (1898).

From his own observations, and from those of Wakeman (*loc. cit.*), he concludes that the relation

$$\frac{\mu_v \text{H}_2\text{O}}{\mu_v \text{H}_2\text{O} \cdot \text{Alc.}} = \text{constant}$$

holds, being independent of both temperature and concentration; that is, the conductivities compared are approaching a limiting value at the same rate, and either the dissociation is the same, in the cases compared, or, for mixtures of alcohol and water, conductivity is not a direct measure of dissociation. Cohen is inclined to the latter view.

Walker and Hambly¹ studied the conductivity of diethylammonium hydrochloride in mixtures of water and ethyl alcohol.

Hantzsch² made interesting applications of results obtained by studying conductivities in various mixtures.

Tijmstra³ investigated the conductivities of solutions obtained by the action of mixtures of methyl or ethyl alcohol and water on sodium. In the case of the mixtures of methyl alcohol and water the minimum was observed.

Roth⁴ made a careful study of the conductivity of potassium chloride in mixtures of ethyl alcohol and water containing 8 and 20 per cent alcohol by weight. He found that the relation given by Wakeman (*loc. cit.*) holds, while that given by Cohen (*loc. cit.*) does not. The quotient

$$\frac{\mu_v \text{H}_2\text{O}}{\mu_v \text{H}_2\text{O} \cdot \text{Alc.}}$$

was found to decrease with increasing dilution, and with increase of the amount of alcohol in the mixture. This, Roth thinks, may indicate a decrease in dissociation. The relation given by Arrhenius (*loc. cit.*) was also found to be valid.

The work of Wolf⁵ and of Rudorf⁶ needs no consideration here.

¹ J. Chem. Soc., 71, 61 (1899).

² Ztschr. anorg. Chem., 25, 332 (1900); Ber. d. chem. Ges., 35, 1001 (1902).

³ Proc. Kon. Akad. te Amsterdam, 1903, p. 104.

⁴ Ztschr. phys. Chem., 42, 209 (1903).

⁵ *Ibid.*, 40, 222 (1902).

⁶ *Ibid.*, 43, 257 (1903).

Jones and Lindsay¹ extended the work of Zelinsky and Krapiwins, and of Cohen. The solvents used were water, methyl, ethyl, and isopropyl alcohols, and binary mixtures of these liquids. The salts employed were potassium, cadmium and strontium iodides, ammonium bromide, and lithium nitrate. The result was to show that the occurrence of the minimum is more or less general. Jones and Lindsay worked at two temperatures, 0° and 25°, and showed that in some cases, though the minimum does not occur at the higher temperature, it does occur at the lower one. They also showed that the effect of increase in temperature upon the minimum is to shift it toward a mixture containing a larger per cent of alcohol.

The first part of this work is a continuation of the investigation of Jones and Lindsay.

PART I.

EXPERIMENTAL.

Apparatus.

The Kohlrausch method of measuring conductivity was used throughout this investigation. The bridge-wire was of "manganin." The resistance coils, manufactured by Leeds & Co., were guaranteed to be accurate to within 0.04 per cent. The conductivity cells were of the form used by Jones and Lindsay. The constants of these were determined by means of N/50 and N/500 solutions of potassium chloride. Cells used to determine conductivities of the solvent and of highly diluted solutions were treated in the manner recommended by Whetham.² The electrodes were first coated with platinum black in the usual manner, and were afterwards heated to a high temperature in the flame of a blast-lamp. It was found, as Whetham states, that the usual coating of platinum black, in spite of careful and long-continued washing, retains traces of salt that subsequently pass slowly into solution. The oxidizing action of the platinum black is also avoided by this treatment. For the purposes mentioned,

¹ Am. Chem. J., **28**, 329 (1902).

² Phil. Trans., **94**, (A), 321 (1900); Ztschr. phys. Chem., **33**, 346 (1900).

electrodes of this kind cannot be too highly recommended. The tone-minimum in the telephone is fully as good as with the ordinary type of electrode.

The 25° thermostat was of the usual (Ostwald) form, and the stirrer was driven by a small hot-air motor. The zero bath was of the type used by Jones and Lindsay, consisting of an outer and inner vessel. The inner vessel and the annular space between the two were filled with finely crushed ice. The outer portion of ice was moistened with a small quantity of distilled water, and to the ice in the inner vessel about an equal weight of water was added. By the foregoing means the temperature of a cell immersed in the ice and water of the inner vessel could be kept for any desired period at 0°.02 to 0°.05 C.

The measuring flasks, pipettes, and burettes were carefully calibrated.

Solvents.

The water used was purified in the following manner: Ordinary distilled water, after addition of potassium dichromate and sulphuric acid, was redistilled. The distillate was again distilled from chromic acid into, and then from, a solution of barium hydroxide. Where the conductivity of the water thus obtained was above 2×10^{-6} , it was redistilled. In many cases the conductivity was much less than this value.

The methyl and ethyl alcohols were the purest commercial preparations obtainable. Each was subjected to the same treatment. The commercial alcohol was dehydrated by standing in contact with freshly burned lime for several weeks. From this it was distilled, and then allowed to stand over dehydrated copper sulphate for a week or more. When required for use, it was distilled from the copper sulphate, small quantities of sodium being added, and precautions were taken to protect the distillate from access of moisture.

The conductivity of the methyl alcohol thus obtained was usually from 1 to 2×10^{-6} . That of the ethyl alcohol was less.

The acetic acid used was obtained from Bender and Hobein,

and was designed for cryoscopic work. The amount of water contained in it was determined, as suggested by Rudolf, by observation of its freezing-point. Its conductivity was less than 2×10^{-6} .

Method of Preparing the Solutions.

The mixtures of solvents were prepared as follows: n cc. of alcohol, for example, were diluted to, say, 100 cc. This is designated as a mixture of " n " per cent alcohol.

Calibrated flasks were used for the dilutions and the temperature was kept to within a few tenths of a degree of the temperature of calibration.

In making up the solutions, the exact amount of the salt in question was put into a measuring-flask, and after addition of a portion of the solvent, the substance was dissolved and the flask filled to the mark. Here also the temperature was kept under control.

Usually, the original solutions were $N/16$ or $N/32$. From these others were made by adding the solvent to a measured portion of the solution. Where the quantity to be used would be too small to be measured with reasonable accuracy, one of the intermediate solutions was taken as a starting-point for further dilution.

Conductivity Measurements.

The constants of the cells used were determined or checked at intervals of a few days. For each conductivity determination from three to seven or eight different resistances were used. The values given in the tables are, therefore, the mean of several determinations. Conductivities throughout are molecular conductivities.

Cadmium Iodide.

The cadmium iodide used was a preparation from Kahlbaum, used by Jones and Lindsay in their work.

Jones and Lindsay measured the conductivity of cadmium iodide in water, methyl alcohol, and mixtures at 25° only. The minimum was not observed. It seemed desirable, therefore, to complete the study of the compound.

The cadmium iodide was dried by being allowed to stand in a desiccator over calcium chloride for a week or more. At first the attempt was made to dry it by prolonged heating in an air-bath at 70° to 80° . It was found that when thus treated, the salt assumed a pinkish hue, which immediately gave place to the pinkish-white of the salt in the ordinary condition when a small quantity of water was added. No mention of this color change can be found in the literature. Though no traces of decomposition could be detected, the other method of drying was chosen. The original solutions were made by direct weighing.

Table I.—Conductivity of Cadmium Iodide in Water at 0° and at 25° .

v .	$\mu_v 0^{\circ}$.	$\mu_v 25^{\circ}$.	Temperature coefficient.
16	31.16	62.86	1.268
32	40.07	81.82	1.670
64	51.93	107.77	2.114
128	63.85	130.24	2.666
256	76.54	155.55	3.160

Table II.—Conductivity of Cadmium Iodide in 25 Per Cent Methyl Alcohol at 0° and at 25° .

v .	$\mu_v 0^{\circ}$.	$\mu_v 25^{\circ}$.	Temperature coefficient.
16	14.57	33.83	0.770
32	17.68	42.10	0.977
64	22.68	55.02	1.294
128	28.59	70.22	1.665
256	35.36	87.31	2.078

Table III.—Conductivity of Cadmium Iodide in 50 Per Cent Methyl Alcohol at 0° and at 25° .

v .	$\mu_v 0^{\circ}$.	$\mu_v 25^{\circ}$.	Temperature coefficient.
16	9.96	20.82	0.434
32	11.23	24.21	0.519
64	14.21	31.25	0.682
128	18.92	41.61	0.908
256	21.58	51.4	1.193

Table IV.—Conductivity of Cadmium Iodide in 75 Per Cent Methyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	8.94	15.78	0.274
32	9.71	17.08	0.295
64	11.24	20.08	0.354
128	14.37	25.68	0.452
256	18.58	33.52	0.598

Table V.—Conductivity of Cadmium Iodide in 100 Per Cent Methyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	10.96	13.39	0.097
32	11.55	14.51	0.118
64	12.66	14.83	0.087
128	13.69	16.82	0.124
256	17.62	20.01	0.096

Table VI.—Comparison of Conductivities at 0°.

<i>v.</i>	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
16	31.16	14.57	9.96	8.94	10.96
32	40.07	17.68	11.23	9.71	11.55
64	51.93	22.68	14.21	11.28	12.66
128	68.53	31.09	18.92	14.37	13.69
256	76.54	35.36	21.58	18.58	17.62

Table VII.—Comparison of Conductivities at 25°.

<i>v.</i>	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
16	62.86	33.83	20.82	15.78	13.39
32	81.82	42.10	24.21	17.08	14.51
64	104.77	55.02	31.25	20.08	14.83
128	130.24	70.22	41.61	25.68	16.82
256	155.55	87.31	51.40	33.52	20.01

Table VIII.—Conductivity of Cadmium Iodide in 25 Per Cent Ethyl Alcohol at 25°.

<i>v.</i>	μ_v 25°.
16	26.97
32	34.90
64	44.21
128	54.54
256	69.71

Table IX.—Conductivity of Cadmium Iodide in 50 Per Cent Ethyl Alcohol at 25°.

<i>v.</i>	μ_v 25°.
16	14.03
32	16.19
64	18.93
128	25.66
256	34.89

Table X.—Conductivity of Cadmium Iodide in 75 Per Cent Ethyl Alcohol at 25°.

<i>v.</i>	μ_v 25°.
16	9.43
32	9.52
64	10.94
128	12.27
256	15.16

Table XI.—Conductivity of Cadmium Iodide in 100 Per Cent Ethyl Alcohol at 25°.

<i>v.</i>	μ_v 25°.
16	2.29
32	2.30
64	2.32
128	2.39
256	2.66

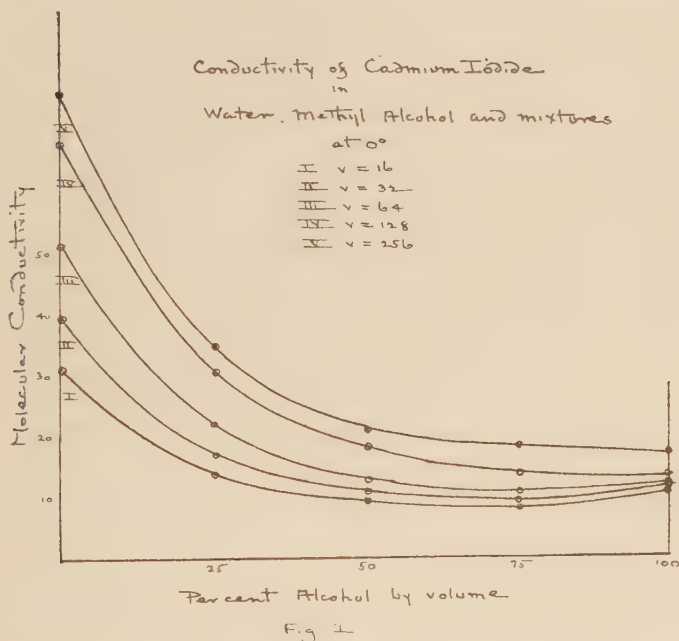
Table XII.—Comparison of Conductivities at 25°.

<i>v.</i>	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent C ₂ H ₅ OH.
16	62.86	26.97	14.03	9.43	2.29
32	81.82	34.90	16.19	9.52	2.30
64	104.77	44.21	18.93	10.94	2.32
128	130.24	54.54	25.66	12.27	2.39
256	155.55	69.71	34.89	15.16	2.66

From the data given, especially in Tables VI. and VII., it is seen that cadmium iodide does not show the minimum in mixtures of methyl alcohol and water at 25°. At 0°, however, in a 75 per cent mixture, at volumes 16, 32, and 64, the minimum appears. Beyond these concentrations it disappears.

In various mixtures of ethyl alcohol and water at 25° (Table XII.) no minimum appears, although the values observed are in all cases less than would be expected from the rule of averages.

The results are plotted as curves in Figs. I. and II.,



the ordinates being conductivities, and the abscissæ representing the per cent by volume of alcohol.

Sodium Iodide.

The sodium iodide used was a preparation that had been carefully purified by Jones and Lindsay.

The salt was dried in an air-bath for three days at a temperature of 110° to 130°. This prolonged treatment was found necessary to bring it to constant weight.

The original solutions were made up by direct weighing.

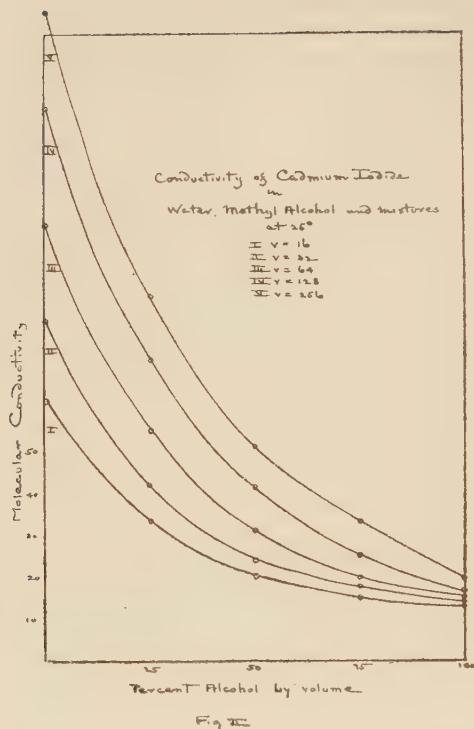


Table XIII.—Conductivity of Sodium Iodide in Water at 0° and at 25°.

v .	$\mu_v 0^\circ$.	$\mu_v 25^\circ$.	$\mu_v 25^\circ(0)$.	Temperature coefficient.
32	57.46	106.0	105.7	1.942
64	59.37	109.35	109.3	2.000
128	60.71	112.44	112.3	2.069
256	62.35	115.5	115.2	2.126
512	64.28	118.08	117.9	2.152

The values in the last column are those given by Ostwald.¹ The agreement is seen to be quite satisfactory.

¹ Ztschr. phys. Chem., I, 74 (1887).

Table XIV.—Conductivity of Sodium Iodide in 25 Per Cent Methyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
32	33.63	70.62	1.48
64	34.68	72.77	1.52
128	35.63	73.78	1.53
256	36.73	74.32	1.504
512	37.83	74.98	1.49

The values at 0° are uncorrected for the conductivity of the solvent.

Table XV.—Conductivity of Sodium Iodide in 50 Per Cent Methyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
32	27.91	57.18	1.171
64	28.73	58.30	1.183
128	29.04	59.16	1.205
256	30.32	60.87	1.232
512	32.08	61.62	1.181

Table XVI.—Conductivity of Sodium Iodide in 75 Per Cent Methyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
32	31.70	56.50	0.992
64	33.08	59.47	1.056
128	34.16	61.49	1.093
256	34.72	62.74	1.121
512	35.00	63.77	1.151

Table XVII.—Conductivity of Sodium Iodide in 100 Per Cent Methyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
32	51.09	72.03	0.838
64	55.95	77.63	0.867
128	58.89	82.70	0.955
256	61.02	86.19	1.009
512	62.56	88.27	1.026

Table XVIII.—Comparison of Conductivities at 0°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
32	57.46	33.63	27.91	31.70	51.09
64	59.37	34.68	28.73	33.08	55.95
128	60.71	35.63	29.04	34.16	58.89
256	62.35	36.73	30.32	34.72	61.02
512	64.28	37.83	32.08	35.00	62.56

Table XIX.—Comparison of Conductivities at 25°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
32	106.0	70.62	57.18	56.50	72.03
64	109.35	72.77	58.30	59.47	77.63
128	112.44	73.78	59.16	61.49	82.76
256	115.49	74.33	60.87	62.74	86.19
512	118.08	74.98	61.62	63.77	88.27

From the data given in Tables XVIII. and XIX., and from the curves plotted in the manner already indicated (Fig. III.), it is evident that sodium iodide exhibits the minimum

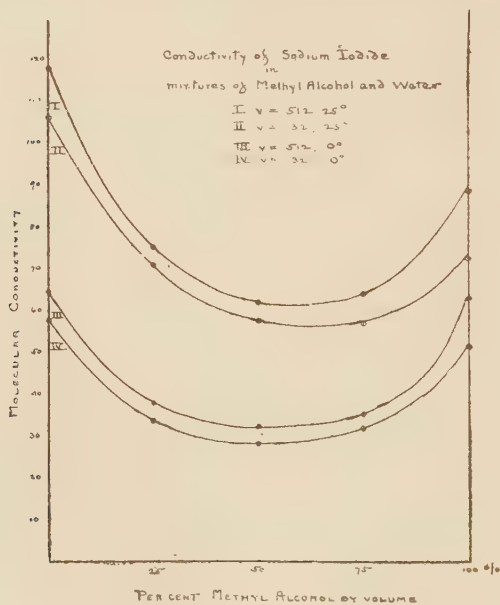


Fig. III.

in mixtures of methyl alcohol and water. Only two dilutions at the two temperatures of observation have been plotted as the curves would be too close together if all were shown.

The minimum, as Jones and Lindsay have observed in other cases, is more pronounced at 0° than at 25° . Further, the shifting effect of change of temperature and of concentration, also observed by Jones and Lindsay, appears at 25° , $v = 32$. The minimum occurs in a 75 per cent mixture; beyond this dilution the minima occur solely in the 50 per cent mixture. At 0° the minimum appears to be exhibited in the 50 per cent mixture alone.

Calcium Nitrate.

It was thought that the study of a ternary salt might prove interesting. Jones and Lindsay had already made a study of strontium iodide, and had found it to exhibit the same phenomena as did binary salts.

The calcium nitrate used was a preparation from Kahlbaum. It was found to be particularly difficult to dehydrate. Heating for several days at a temperature of 130° to 140° was necessary to bring it to constant weight. This treatment caused no perceptible decomposition. All original solutions were made by direct weighing.

Table XX.—Conductivity of Calcium Nitrate in Water at 0° and at 25° .

v .	$\mu_v 0^\circ$.	$\mu_v 25^\circ$.	Temperature coefficient.
16	94.33	177.56	3.329
32	102.47	189.45	3.440
64	108.35	199.24	3.636
128	113.59	209.93	3.854
256	118.02	215.93	3.916

Table XXI.—Conductivity of Calcium Nitrate in 25 Per Cent Methyl Alcohol at 0° and at 25° .

v .	$\mu_v 0^\circ$.	$\mu_v 25^\circ$.	Temperature coefficient.
16	53.17	111.45	2.331
32	57.30	120.63	2.533
64	59.81	128.95	2.766
128	63.39	136.81	2.937
256	66.19	141.45	3.010

Table XXII.—Conductivity of Calcium Nitrate in 50 Per Cent Methyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	41.07	79.04	1.518
32	44.70	90.11	1.816
64	49.15	98.35	1.968
128	53.94	103.68	1.990
256	54.82	109.19	2.175

Table XXIII.—Conductivity of Calcium Nitrate in 75 Per Cent Methyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	39.59	70.06	1.219
32	43.60	80.16	1.462
64	48.85	89.98	1.645
128	51.90	97.72	1.883
256			

Table XXIV.—Conductivity of Calcium Nitrate in 100 Per Cent Methyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16		32.79	
32	31.30	41.88	0.423
64	37.27	50.79	0.541
128	46.66	60.52	0.555
256	55.17	73.98	0.752

Table XXV.—Comparison of Conductivities at 0°.

<i>v.</i>	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
16	94.33	53.17	41.07	39.59	
32	102.47	57.30	44.70	43.60	31.30
64	108.35	59.81	49.15	48.85	37.27
128	113.59	63.39	53.94	51.90	46.66
256	118.02	66.19	54.82		55.17

Table XXVI.—Comparison of Conductivities at 25°.

<i>v.</i>	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
16	177.56	111.45	79.04	70.06	32.79
32	189.45	120.63	90.11	80.16	41.88
64	199.24	128.95	98.35	89.98	50.79
128	209.93	136.81	103.68	97.72	60.52
256	215.93	141.45	109.19		73.98

Table XXVII.—Conductivity of Calcium Nitrate in 25 Per Cent Ethyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	38.80	92.93	2.065
32	41.84	100.56	2.359
64			
128	48.02	112.93	2.596
256	50.26	119.04	2.750

Table XXVIII.—Conductivity of Calcium Nitrate in 50 Per Cent Ethyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	23.7	60.43	1.469
32	25.89	65.30	1.576
64	27.37	69.83	1.698
128	28.83	74.13	1.812
256	30.30	78.31	1.920

Table XXIX.—Conductivity of Calcium Nitrate in 75 Per Cent Ethyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	19.13	39.08	0.798
32	21.41	44.57	0.926
64			
128	26.71	56.08	1.175
256	28.61	60.79	1.287

Table XXX.—Conductivity of Calcium Nitrate in 100 Per Cent Ethyl Alcohol at 0° and at 25°.

<i>v.</i>	μ_v 0°.	μ_v 25°.	Temperature coefficient.
16	4.89	7.08	0.088
32	7.11	9.57	0.098
64	8.59	12.43	0.153
128	10.74	15.47	0.189
256	12.48	18.57	0.244

Table XXXI.—Comparison of Conductivities at 0°.

<i>v.</i>	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent C ₂ H ₅ OH.
16	94.33	38.80	23.7	19.13	4.89
32	102.47	41.84	25.89	21.41	7.11
64	108.35		27.37		8.57
128	113.59	48.02	28.83	26.71	10.74
256	118.02	50.26	30.30	28.61	12.48

Table XXXII.—Comparison of Conductivities at 25°.

v.	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent C ₂ H ₅ OH.
16	177.56	92.93	60.43	39.08	7.08
32	189.45	100.56	65.30	44.57	9.57
64	199.24		69.83		12.43
128	207.93	112.93	74.13	56.08	15.47
256	215.93	119.04	78.31	60.79	18.57

From the data given in Tables XXV., XXVI., XXXI., and XXXII., it is evident that calcium nitrate in no case exhibits the minimum. The conductivities are always less than the proper average.

The relation found by Wakeman,¹

$$\frac{\Delta}{p(100-p)} = \text{const.},$$

does not hold in the cases thus far studied; nor does that found by Cohen.¹

Hydrochloric Acid.

In the study of hydrochloric acid the solutions were made as follows: The solvent was prepared in the usual manner. Into a portion of the solvent, kept cool by ice, dry hydrochloric acid gas was passed. This was obtained by allowing concentrated sulphuric acid to drop slowly from a dropping-funnel into pure, aqueous, hydrochloric acid. The gas was dried by passing through two gas-washing bottles containing concentrated sulphuric acid. The vessel containing the solvent into which the gas was passed was protected from extraneous moisture by a drying-tube containing phosphorus pentoxide.

The strength of the original solution was determined volumetrically by means of a standard solution of ammonium hydroxide, methyl orange being used as the indicator. From this solution the dilutions were made, control determinations being carried out on some of them because only the tolerably dilute ones in mixtures and in pure methyl alcohol were found to be stable.

¹ *Loc. cit.*

The composition of the 69.75 per cent mixture was determined by means of its specific gravity.

Table XXXIII.—Conductivity of Hydrochloric Acid in 50 Per Cent Methyl Alcohol at 25°.

$v.$	$\mu_v 25^\circ.$
33.05	172.45
132.21	166.09
264.42	165.30
528.83	155.29

Table XXXIV.—Conductivity of Hydrochloric Acid in 69.75 Per Cent Methyl Alcohol at 0° and at 25°.

$v.$	$\mu_v 0^\circ.$	$\mu_v 25^\circ.$
44.67	63.83	116.0
92.42	67.06	123.77
178.75	66.49	117.8
357.5	64.66	118.1
714.72	66.19	116.87

Table XXXV.—Conductivity of Hydrochloric Acid in 90 Per Cent Methyl Alcohol at 0° and at 25°.

$v.$	$\mu_v 0^\circ.$	$\mu_v 25^\circ.$
31.53	46.59	73.79
63.07	47.60	76.19
157.67	51.84	84.27
252.28	51.84	84.27
252.28	51.85	84.38
504.56		84.22

Table XXXVI.—Conductivity of Hydrochloric Acid in 100 Per Cent Methyl Alcohol at 0° and at 25°.

$v.$	$\mu_v 0^\circ.$	$\mu_v 25^\circ.$
8.42	67.36	95.83
32.8	77.06	110.50
130.26	79.84	118.79
481.44	89.79	129.87
2104.0	95.46	133.44

A consideration of the results, Tables XXXIII., XXXIV., XXXV., XXXVI., shows that in certain cases they are irregular and unexpected. In the 50 per cent mixture the conductivity falls from the first dilution, which is analogous to

what has been observed for hydrochloric acid in ether and isoamyl alcohol by Cattaneo¹ and Kablukoff,² and for sulphuric acid in acetic acid by Jones.³ In all these cases the molecular conductivities decreased with decreasing dilution.

In the 69.75 per cent a maximum is reached at $v = 92.42$ at both 0° and 25° . From this point on, the conductivities decrease slightly. However, at 0° the mean of the last four conductivities, including the maximum, differs from the maximum value by only 1.5 per cent.

In the 90 per cent mixture the results are perfectly regular, and, what is surprising, a limiting value is reached at $v = 157.67$.

In methyl alcohol the results are also regular, but there is no indication of a maximum value for conductivity. The values found agree in most cases very well with those of Carrara,⁴ whose results are also irregular.

It is seen, further, that hydrochloric acid shows the minimum (Fig. IV.) in both the 69.75 per cent and 90 per cent mixtures. At 25° the minimum appears in the former after the dilution $v = 178.75$. At 0° it appears at all dilutions. Carrara⁴ also observed the minimum in the case of hydrochloric acid, finding it to occur in methyl alcohol containing about 2 per cent of water.

The conductivity curves (Fig. IV.) for $v = 33$ are plotted.

Sodium Acetate in Mixtures of Acetic Acid and Water.

Thus far we have been concerned with conductivities in mixtures of alcohol and water. An investigation by Jones and Murray⁵ seemed to make it advisable to study conductivities in other mixtures—notably of acetic or formic acid and water.

As stated, the acetic acid used was a preparation intended for cryoscopic work. The amount of water in this acid was

¹ Atti. R. Acc. delle Sc., Torino, **28**, 329; Rend. R. Accad. dei Lincei, (5), **2**, 295.

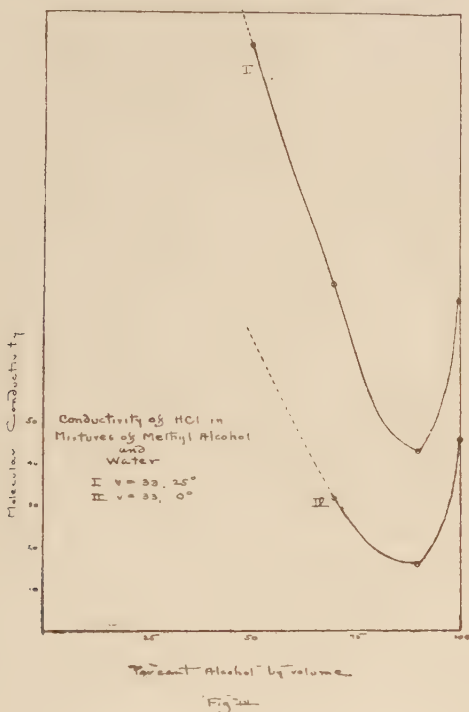
² Ztschr. phys. Chem., **4**, 431 (1889).

³ Am. Chem. J., **16**, 1 (1894).

⁴ Gazz. chim. ital., **26**, (1), 119 (1896).

⁵ Am. Chem. J., **30**, 193 (1903).

determined by means of its freezing-point, as recommended by Rüdorff.¹ The substance froze at $15^{\circ}.47$. From the tables given by Rüdorff (*loc. cit.*) it was found to contain in 100 parts



by weight, 0.6 part by weight of water. Knowing the composition of the acid, the proper amounts to be used in making the mixtures could be calculated.

The acid was partially frozen and the liquid portion rejected. After melting the solid acid the process was repeated. The specimen thus obtained was used for the conductivities in the pure solvent. Owing to inevitable exposure to the moisture of the air, it was not thought profitable to try to remove the last traces of moisture.

In this part of the problem new complications arose, since acetic acid, in aqueous solution, conducts the current.

¹ Ber. d. chem. Ges., 3, 390 (1870).

The specific conductivity of the solvent (containing 25, 50, 75, and 100 per cent by volume of acetic acid) was determined; then that of the solution in question. The difference between the latter and the former was multiplied by the volume to give the (apparent) molecular conductivity.

The sodium acetate used was a specimen of the fused salt obtained from Kahlbaum. It was dried for two days in an air-bath at 120° to 130°. The original solutions were made up by direct weighing.

Table XXXVII.—Conductivity of Sodium Acetate in 25 Per Cent Acetic Acid at 25°.

Specific conductivity of solvent = 1.631.

<i>v.</i>	Specific conductivity of solution.	μ_v 25°.
32	2.040	17.89
64	1.469	—10.37

Table XXXVIII.—Conductivity of Sodium Acetate in 50 Per Cent Acetic Acid at 25°.

Specific conductivity of solvent = 0.8584.

<i>v.</i>	Specific conductivity of solution.	μ_v 25°.
32	1.388	16.84
64	0.9263	4.36
128	0.8986	5.15

Table XXXIX.—Conductivity of Sodium Acetate in 75 Per Cent Acetic Acid at 25°.

Specific conductivity of solvent = 0.0558.

<i>v.</i>	Specific conductivity of solution.	μ_v 25°.
32	0.7050	20.77
64	0.4446	24.87
128	0.2999	31.24

Table XL.—Conductivity of Sodium Acetate in Acetic Acid at 25°.

Conductivity of solvent = 1×10^{-6} .

<i>v.</i>	Specific conductivity of solution.	μ_v 25°.
32	0.00418	0.134
64	0.00236	0.161
128	0.00129	0.165

On examination, the results are seen to be irregular, and no conclusions can be drawn from them. In the 25 per cent mixture as $v = 64$, the molecular conductivity is apparently negative. This, of course, means nothing more than that the specific conductivity of the solvent is greater than that of the solution. Only in the 75 per cent mixture is there any regularity observed. Here the (apparent) molecular conductivities increase with decreasing concentration.

In the pure solvent the conductivities are so small as almost to be negligible. This is not surprising. Wakeman¹ has determined the conductivity of hydrochloric acid in acetic acid, and has found it to be exceedingly small. For example, for $v = 98.56$ μ_v was found to be 1.78.

The irregular results in mixtures of acetic acid and water are to be explained as being due to mutual isohydric influence of dissolved substance and solvent. The dissociation of the sodium acetate is driven back by the acetic acid, and *vice versa*. This influence is most marked where the dissociation of each separately would be greatest, *i. e.*, in mixtures of lower per cent of acetic acid, and of minimal concentration of sodium acetate.

Since these phenomena have no direct connection with the problem in hand, no further discussion is necessary, especially as the question has been treated by Wolf² and by Rudolf.²

PART II.

Dissociation in Fifty Per Cent Methyl Alcohol.

It has been seen that in the case of hydrochloric acid in mixtures of methyl alcohol and water, limiting values for conductivity are reached at a smaller dilution than in either water or methyl alcohol. It is important to see whether this is a general phenomenon.

The limiting values in the case of sodium and potassium iodides and potassium bromide were determined. Throughout this part of the work the utmost care was taken in the preparation of solvents and solutions and in making the dilutions. The cells used were standardized before and after each

¹ Ztschr. phys. Chem., **15**, 181 (1894).

² *Loc. cit.*

series of measurements. The conductivity of the solvent was carefully determined and the necessary corrections were made. The water and the methyl alcohol used had a conductivity of not over 1×10^{-6} . All results given are the mean of from five to ten different values.

Potassium Iodide.

The potassium iodide was a preparation furnished by Kahlbaum. The flame test showed that no appreciable impurity was present. The salt was dried at 100° to 110° for a day. The values obtained were :

v .	$\mu_v 25^{\circ}$.
400	69.29
2000	70.58
4000	70.60

The value for the conductivity at $v = 400$ agrees with the (interpolated) value obtained by Zelinsky and Krapivin,¹ and my results may therefore be incorporated with theirs. This has been done in the following table. The degree of dissociation has been calculated for each dilution. Included in the table, for comparison, are similar values calculated from data obtained by Ostwald¹ for potassium iodide in water, and from data given by Carrara¹ for potassium iodide in methyl alcohol.

Table XLI.—Conductivity of Potassium Iodide in Water, Methyl Alcohol, and 50 Per Cent Methyl Alcohol at 25° .

	H ₂ O.	50 Per cent CH ₃ OH.	CH ₃ OH.
v .	$\mu_v 25^{\circ}$.	$\mu_v 25^{\circ}$.	$\mu_v 25^{\circ}$.
16	124.5	62.13	68.14
32	128.5	64.37	74.42
64	130.5	66.01	79.85
128	133.0	67.45	84.70
256	135.8	68.28	88.25
400		69.20	
512	137.9	69.65	90.82
1024	140.9	70.55	93.07
2000		70.58	
4000		70.60	
∞	142.6	70.58	97.63

¹ *Loc. cit.*

The values of the dissociation factors are shown in the following table. From an inspection of the data it is seen that a limiting value for conductivity is reached at a lower dilution in the mixture than in the other solvents.

Table XLII.—Dissociation of Potassium Iodide in Water, Methyl Alcohol, and 50 Per Cent Methyl Alcohol.

	H ₂ O.	50 Per cent CH ₃ OH.	CH ₃ OH.
<i>v.</i>	α .	α .	α .
16	0.873	0.880	0.697
32	0.900	0.912	0.762
64	0.915	0.936	0.818
128	0.931	0.956	0.868
256	0.953	0.968	0.904
512	0.967	0.987	0.931
1024	0.989	1.000	0.954

An inspection of this table shows that, at corresponding dilutions, *dissociation as calculated from conductivity is greater in the mixture than in methyl alcohol or in water.* The only other solvent thus far shown to have a greater dissociation power than water is liquid hydrocyanic acid, as appears from the work of Centnerszwer.¹ Potassium iodide was one of the substances used.

Sodium Iodide.

The sodium iodide was the preparation previously employed. The following measurements were made :

<i>v.</i>	μ_v 25°.
500	60.92
2000	61.72
4000	61.65

Combining these with the values previously obtained and using Carrara's² values for conductivities in water and methyl alcohol, respectively, we have the following :

¹ Ztschr. phys. Chem., **39**, 217 (1902).

² Loc. cit.

Table XLIII.—Conductivity of Sodium Iodide in Water, Methyl Alcohol, and 50 Per Cent Methyl Alcohol at 25°.

v .	H ₂ O. μ_v 25°.	50 Per cent CH ₃ OH. μ_v 25°.	CH ₃ OH. μ_v 25°.
32	106.0	57.18	68.75
64	109.3	58.30	73.11
128	112.4	59.16	77.31
256	115.5	60.87	79.90
512	118.1	61.27	82.15
2000		61.72	
4000		61.65	
∞	121.4	61.68	89.77

It is evident, in this case, that the results are of the same general character as those found for potassium iodide.

Table XLIV.—Dissociation of Sodium Iodide in Water, Methyl Alcohol, and 50 Per Cent Methyl Alcohol.

v .	H ₂ O. α .	50 Per cent CH ₃ OH. α .	CH ₃ OH. α .
32	0.865	0.927	0.766
64	0.901	0.946	0.816
128	0.917	0.959	0.861
256	0.949	0.987	0.890
512	0.971	0.993	0.915
2000		1.000	
4000	1.000	1.000	

Here also, as was found for potassium iodide, the dissociation is greatest in the mixture.

The following measurements were made for potassium bromide in 50 per cent methyl alcohol :

v .	μ_v 25°.
250	65.78
1250	69.26
2500	69.35

At $v = 250$ the dissociation is 0.949 for the mixture.

At $v = 256$ the dissociation is 0.927 for water, 0.806 for methyl alcohol, as calculated from Ostwald's¹ and Carrara's¹ observations.

¹ *Loc. cit.*

Table XLV.—Dissociation of Ammonium Bromide in 50 Per Cent Methyl Alcohol.

<i>v.</i>	50 Per cent CH ₃ OH. <i>α.</i>
16	0.871
32	0.910
64	0.942
128	0.962
256	0.974
512	0.986
1024	1.000

The values for the dissociation constants are seen to be about the same as those for potassium iodide. Data for conductivity in aqueous solution could not be found. The values for methyl alcohol are calculated from Carrara's¹ data ; those for the mixture, from Zelinsky and Krapiwins.¹

Table XLVI.—Dissociation of Ammonium Iodide in 50 Per Cent Methyl Alcohol.

<i>v.</i>	50 Per cent CH ₃ OH. <i>α.</i>
16	0.875
32	0.909
64	0.943
128	0.967
256	0.973
512	0.994
1024	1.000

Here the values are about the same as for ammonium bromide. No reliable data could be found for ammonium iodide in water. The data for the mixture and for methyl alcohol were furnished by Zelinsky and Krapiwins¹ and by Carrara¹, respectively.

From results given by Jones and Lindsay¹ it is possible to calculate the dissociation of lithium nitrate in the 50 per cent mixture at two temperatures, 0° and 25°, assuming that here, as in the other cases, complete dissociation is reached at $v = 1024$. It is known that in aqueous solution complete dissociation is not reached as soon in the case of lithium salts as with potassium or sodium salts. Less value must therefore be attached to the following results :

¹ *Loc. cit.*

Table XLVII.—Dissociation of Lithium Nitrate in 50 Per Cent Methyl Alcohol at 0° and at 25°.

v .	α 0°.	α 25°.
32	0.863	0.862
64	0.899	0.899
128	0.915	0.926
256	0.944	0.964
512	0.963	0.982
1024	1.000	1.000

Values of the dissociation for hydrochloric acid in the 90 per cent and in the 69.75 per cent mixture at 0° and at 25° are also given. It will be remembered that the results in the latter mixture were irregular. No stress can, therefore, be laid upon these figures. We have taken the determinations for $v = 92.4$ as the limiting values in this case.

Table XLVIII.—Dissociation of Hydrochloric Acid in 69.75 Per cent and 90 Per cent Methyl Alcohol, in Water and in Methyl Alcohol.

v .	69.75 Per cent CH ₃ OH.		90 Per cent CH ₃ OH.		H ₂ O.	CH ₃ OH.	v
	α 0°.	α 25°.	α 0°.	α 25°.	α 25°.	α 25°.	
31.5			0.900	0.875	0.909	0.890	37.74
44.67	0.981	0.937				0.916	75.47
63.0			0.919	0.924			
92.42	1.000	1.000				0.972	150.9
158			1.000	1.000			
252			1.000	1.000	0.934		

The values for conductivities in water are taken from Ostwald;¹ those for methyl alcohol from Carrara.²

Here it is observed that the dissociation is greater in the 69.75 per cent mixture than in water at the corresponding dilution. This, however, is not the case for the 90 per cent mixture.

It is also interesting to note that the dissociation is apparently greater at 0° than it is at 25°, and this is true for the 90 per cent mixture, where the results are more reliable than those for the 69.75 per cent mixture.

¹ J. prakt. Chem., 140, 300 (1885).

² Loc. cit.

I have suggested (p. 34) that the dissociation in the 50 per cent mixture may be due in part to the presence of the hydrate $\text{CH}_3\text{OH}, 3\text{H}_2\text{O}$. This compound would be more stable at a lower than at a higher temperature, and would be present at the lower temperature to a greater extent, and therefore the dissociation might be greater. This result should be shown by salts as well as by hydrochloric acid, but data are not at hand for comparison. Jones and Lindsay's values for lithium nitrate are available and have been used (Table XL.). From this table, apparently, the dissociation is greater at the higher temperature. But, as we have said, no final conclusions can be drawn from these data, since we cannot be certain that limiting conductivity values were reached by Jones and Lindsay. In the case of hydrochloric acid, however, they were reached, in at least one instance. Further investigation will be needed to decide this matter.

It is interesting at this point to see whether the hypothesis of Dutoit and Aston¹ is quantitatively true for the cases that have been considered. This hypothesis is that the dissociating power of a solvent is dependent upon its association, as determined by the surface-tension method of Ramsay and Shields.² If the hypothesis holds quantitatively it may be formulated thus:

$$\frac{\alpha}{\alpha'} = \frac{x}{x'},$$

where α and α' are the dissociations of the solutions compared, and x and x' the association factors of the solvents. The relation may be put into the form—

$$\frac{\alpha}{x} = \text{const.}$$

In comparing solutions in different solvents, there should be the same number of gram-molecules of electrolyte dissolved in the same number of gram-molecules of each solvent. Where solutions in water, methyl alcohol, and ethyl alcohol are to be compared, the volumes will have the ratio 18, 40, and 58 approximately.

¹ *Compt. rend.*, **125**, 240 (1897).

² *Ztschr. phys. Chem.*, **12**, 433 (1893).

A comparison is made on this basis, for potassium and sodium iodide in water, and methyl and ethyl alcohols. For the ethyl alcohol solution the dissociation was calculated from the data of Völlmer.¹ The others were taken from the preceding tables.

Table XLIX.— $\frac{\alpha}{x}$ for Potassium and Sodium Iodides in Water and Methyl and Ethyl Alcohols at 25°.

	H ₂ O. $x = 3.68$. Constant.	CH ₃ OH. $x = 3.43$. Constant.	C ₂ H ₅ OH. $x = 2.74$. Constant.	
KI	24.9	25.3	24.9	
NaI	23.5	23.7	23.6	$v = 32, 64, 100$
	24.5	25.1		$v = 64, 128$
KBr	25.8	26.2		$v = 128, 256$

Similarly, assuming that Dutoit and Aston's hypothesis holds for 50 per cent methyl alcohol, we may calculate its degree of association. Taking the value of the constant as 23.6, and the comparable volume for the mixture as 48, from the relation $\frac{\alpha}{x} = 23.6$ we can find x . We have $\frac{93.7}{x} = 23.6$, whence $x = 3.96$.

A mixture of methyl alcohol and water, containing 50 per cent methyl alcohol by volume, has very approximately the composition corresponding to the hydrate CH₃OH, 3H₂O. The existence of alcoholic hydrates has been made probable on other grounds. *It is possible that such hydrates, in virtue of their complexity, have high dissociating power. The greater dissociation found in the 50 per cent mixture may be due to this hydrate, in which four simple molecules combine to form a complex molecule.*

PART III.

ause of the Minimum.

The first observers of the conductivity minimum, Zelinsky and Krapivin, offered no satisfactory explanation. They suggested that it might be connected with the formation of hydrates

¹ Wied. Ann., 52, 328 (1894).

of methyl alcohol. Further than this they did not go. Jones and Lindsay¹ offered the following explanation: "According to the theory of Dutoit and Aston, it is only those substances whose molecules are polymerized that can dissociate dissolved electrolytes. If this be true, it is probable, since those substances which dissociate dissolved electrolytes also show, in general, a normal molecular weight for dissolved non-electrolytes, that this breaking-down of the polymerized molecule can be accomplished best by another associated molecule. From this it follows that the effect of mixing two associated solvents would be to lower the state of association of one or both until a state of equilibrium is reached. Such a mixture would be that of water and either methyl or ethyl alcohol, or a mixture of methyl alcohol and ethyl alcohol. In these cases, since the molecules of the mixture are less associated than those of the constituents, we should expect dissolved electrolytes to show a conductivity lower than that required by the law of mixtures. In every solvent with which we have worked this is exactly what has been observed. In the mixtures of methyl alcohol and water, where the association of the constituents is the greatest, the lowering of conductivity is also the greatest, as would be expected.

In support of the above view that one associated solvent can diminish the association of another associated solvent, we have experimental evidence in the results of freezing-point measurements. The molecular weights of the alcohols in water, as determined by the freezing-point method, are normal, while the surface-tension method of Ramsay and Shields shows, beyond question, that the alcohols are associated compounds.

The effect of temperature on the lowering of the conductivity is in accord with the above suggestion. Since the effect of rise in temperature is to lower the state of aggregation of an associated liquid, it would be expected that at the higher temperature the influence of the solvents on each other would be less than at the lower temperature. That such is the case can be seen by comparing the results at 0° with those at 25°."

¹ *Loc. cit.*

The explanation offered by Jones and Lindsay was later strengthened by an investigation by Jones and Murray.¹ They showed, from a study of the freezing-points of solutions of acetic and formic acids, and water—acetic acid in formic acid, formic acid in acetic acid, acetic acid in water, etc.—that the association of one solvent is apparently diminished by the presence of another associated solvent.

According to the explanation offered by Jones and Lindsay, the chief cause producing the minimum is a diminution of dissociation and consequent decrease in conductivity. I have shown that, in the 50 per cent mixture of methyl alcohol and water, the dissociation, instead of being diminished by the presence of the alcohol (or by bringing together water and the alcohol), is actually increased. This fact alone makes it evident that the explanation offered by Jones and Lindsay does not account for the phenomenon.

Two factors determine conductivity—amount of dissociation and ionic mobility. Decrease in one or both of these produces decrease in conductivity. It has been shown that the decrease in conductivity in question cannot be due to decrease in dissociation. The inevitable conclusion is, then, that it is due to a decrease in ionic mobility.

A complete explanation of the minimum in conductivity will have to account for the following facts:

1. The effect itself.
2. The fact that the effect is more pronounced at a lower temperature than at a higher.
3. The fact that rise in temperature (and in some cases increase in concentration) shifts the minimum toward a mixture containing a larger per cent of alcohol.

There is a close connection between the viscosity or fluidity of a solvent and the conductivity of electrolytes when dissolved in the solvent. The greater the fluidity, or the less the viscosity, other things being equal, the greater is the conductivity. This close relationship is shown by the fact that, for certain aqueous solutions, the temperature coefficients of conductivity and of fluidity are identical. The connection

¹ *Am. Chem. J.*, **30**, 193 (1903).

between conductivity and fluidity, or viscosity, will be considered in detail in the concluding part of this dissertation.

The investigations of Jones and Lindsay, Zelinsky and Krapivin, and this investigation have had to do with conductivities in mixtures of solvents. Numerous researches have been made on the viscosities of mixtures of liquids, notably by Graham,¹ Noack,² Pagliani and Battelli,³ and Traube.⁴ All of these workers have found that, in the case of mixtures of various alcohols and water, the viscosity of the mixture is much greater than would be expected from the law of averages. This is best shown graphically by plotting the viscosities as ordinates and the percentage composition of the mixtures as abscissae. The viscosity curve is seen to pass through a maximum. The fluidity of a liquid is the reciprocal of its viscosity. If, therefore, we show graphically the variations in fluidity as the variations in viscosity were shown, the fluidity curve is seen to pass through a minimum. In all cases, of course, the fluidity is less than a proper average.

The mixtures in which the minimum of conductivity is found to occur are approximately the mixtures in which this minimum of fluidity appears. The explanation of the conductivity minimum that is offered is the following :

The minimum in conductivity is caused primarily by the great decrease of fluidity resulting when the two components of the solvent mixture are brought together.

From the results of Pagliani and Battelli⁵ and of Traube⁶ I have calculated the various fluidities of mixtures of methyl and ethyl alcohol and water, for the temperatures 0°, 10°, 20°, and 30°, and have plotted the fluidity curves (Figs. V. and VI.) in the manner indicated.

From a consideration of these curves it is evident that, for mixtures of water and methyl alcohol at 0°, the minimum of

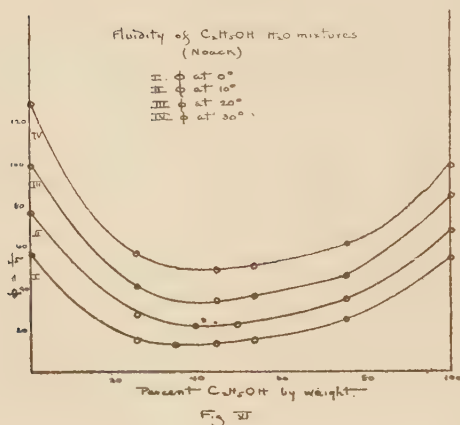
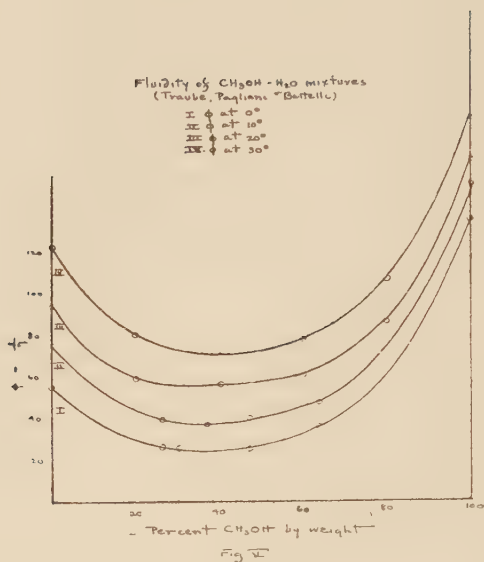
¹ Ann. Chem. (Liebig), **120**, 90 (1861).

² Wied. Ann., **27**, 289 (1886).

³ Atti. di R. Ac. delle Sc. d. Torino., **20**, 607 (1885).

⁴ Ber. d. chem. Ges., **19**, 871 (1889).

⁵ Loc. cit.



fluidity occurs in a mixture containing 31 per cent methyl alcohol by weight (37 per cent by volume); at 20° the minimum occurs in a 40 per cent mixture (46 per cent by volume). Further, the drop in fluidity is more pronounced the lower the temperature.

For the mixtures of ethyl alcohol and water, at 0° , the minimum occurs in a 34 per cent (40 per cent by volume) mixture. At 30° it is found in a 50 per cent (56 per cent) mixture. The minimum is also more pronounced at the lower temperature.

It should be noted that the change in fluidity is very small over a considerable range—particularly in the case of mixtures of ethyl alcohol and water. At 30° the change of fluidity between 30 per cent and 60 per cent is very slight.

We have here fulfilled all the requirements of a complete explanation of the minimum. The two phenomena are parallel throughout—they are either causally related or have a common cause. The former supposition is much more probable, particularly in the light of the admitted connection between conductivity and fluidity.

The parallelism may be summed up as follows :

1. The conductivity minimum is found to be accompanied by a minimum in fluidity.
2. Both minima are more pronounced at lower temperatures, and both occur at approximately the same points.
3. The effect of increase in temperature is the same upon both minima—there is a shifting towards a mixture containing a greater per cent of alcohol, but the fluidity minimum, so to speak, lags behind the conductivity minimum.

For comparison, the following tables are taken from the work of Jones and Lindsay :

Table L.—Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of These Solvents at 0° .

v.	0 Per cent.	20 Per cent.	40 Per cent.	50 Per cent.	65 Per cent.	80 Per cent.	100 Per cent CH ₃ OH.
64	74.09		35.48	33.73	35.12	39.03	59.32
128	76.41	47.26	35.92	34.44	35.71	40.51	63.88
256	77.01	47.79	36.52	35.13	36.49	41.83	67.73
512	78.01	48.45	37.02	36.05	37.23	43.23	69.85
1024	77.96	49.07	37.85	36.76	37.75	44.45	71.23

Table LI.—Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of These Solvents at 25°.

<i>v.</i>	0 Per cent.	20 Per cent.	40 Per cent.	50 Per cent.	65 Per cent.	80 Per cent.	100 Per cent CH ₃ OH.
64	132.1	91.91	72.14	67.46	65.04	67.78	82.87
128	135.4	93.78	73.69	68.79	67.25	70.33	88.49
256	138.0	95.64	75.14	70.37	68.78	71.83	93.73
512	139.6	97.12	76.25	71.72	70.00	73.16	98.36
1024	140.7	98.10	77.68	72.57	70.94	74.81	102.0

It is seen that at 0° the minimum of conductivity occurs in a 50 per cent mixture; the fluidity minimum occurs in a 40 per cent mixture. At 25° the minima occur in 65 per cent and 56 per cent mixtures, respectively.

Strontium iodide also presents a good example of the shifting of the minimum, as the following tables from Jones and Lindsay's work show :

Table LII.—Comparison of the Molecular Conductivity of Strontium Iodide in Water, Methyl Alcohol, and Mixtures of These Solvents at 0°.

<i>v.</i>	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
32	113.1	63.00	50.19	55.53	75.82
64	117.7	66.05	52.61	59.24	85.01
128	122.1	68.62	55.05	62.85	94.76
256	126.0	70.98	57.18	66.68	104.4
512	129.8	73.10	59.51	69.98	114.0
1024	132.6	75.51	61.03	73.22	123.4

Table LIII.—Comparison of the Molecular Conductivity of Strontium Iodide in Water, Methyl Alcohol, and Mixtures of These Solvents at 25°.

<i>v.</i>	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
32	205.3	131.3	103.8	98.09	101.4
64	214.5	138.5	109.9	104.8	115.3
128	223.1	145.3	115.3	111.4	128.6
256	231.8	152.3	120.1	118.0	141.4
512	240.2	157.4	124.3	124.8	153.9
1024	245.9	161.9	128.5	131.4	166.3

In the case of strontium iodide the real minimum would probably be found in a mixture between the 50 and 75 per cent mixtures.

So, also, in the case of lithium nitrate, as shown in the following tables taken from the work of Jones and Lindsay :

Table LIV.—Comparison of the Molecular Conductivity of Lithium Nitrate in Methyl Alcohol, Water, and Mixtures of These Solvents at 0°.

ν .	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
32	50.00	29.15	23.59	26.67	45.97
64	51.49	29.68	24.49	27.95	50.12
128	52.51	30.15	25.03	28.66	53.95
256	53.40	30.70	25.71	29.51	56.67
512	54.70	31.35	26.35	30.64	60.06
1024	55.30	32.56	27.35	31.91	63.40

Table LV.—Comparison of the Molecular Conductivity of Lithium Nitrate in Methyl Alcohol, Water, and Mixtures of These Solvents at 25°.

ν .	0 Per cent.	25 Per cent.	50 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
32	91.83	60.56	47.87	47.06	63.51
64	94.62	62.16	49.92	49.52	69.32
128	98.00	63.77	51.50	51.64	74.51
256	99.68	64.96	53.57	54.36	80.57
512	101.3	66.78	54.62	56.68	83.31
1024	102.3	69.02	55.60	58.56	86.46

An examination of my own values for sodium iodide (p. 18) shows that at 0° the minimum occurs in the 50 per cent mixture. At 25°, for one dilution, $\nu = 32$; it occurs in the 75 per cent mixture, elsewhere, in the 50 per cent mixture. In all probability the real minimum would be found in an intermediate mixture.

When we attempt a comparison for ethyl alcohol the data are more meager. The minimum was found by Jones and Lindsay to occur only at 0° in the cases studied by them. Their data are given :

Table LVI.—Comparison of the Molecular Conductivity of Ammonium Bromide in Water, Ethyl Alcohol, and a 50 Per Cent Mixture of These Solvents at 0°.

	H ₂ O.	Mixture.	C ₂ H ₅ OH.
<i>v.</i>	μ_v 0°.	μ_v 0°.	μ_v 0°.
64	74.22	19.42	16.71
128	75.23	19.89	18.83
256	76.62	20.09	19.66
512	77.49	20.70	22.66
1024	77.78	21.50	22.88

Table LVII.—Comparison of the Molecular Conductivity of Potassium Iodide in Ethyl Alcohol, Water, and a 50 Per Cent Mixture of These Solvents at 0°.

	H ₂ O.	Mixture.	C ₂ H ₅ OH.
<i>v.</i>	μ_v 0°.	μ_v 0°.	μ_v 0°.
64	74.09	19.26	19.12
128	76.4	19.82	21.36
256	77.01	20.35	22.66
512	78.0	20.92	25.00
1024	77.96	21.43	27.43

Table LVIII.—Comparison of the Molecular Conductivities of Lithium Nitrate at 0°.

	H ₂ O.	50 Per cent mixture.	C ₂ H ₅ OH.
<i>v.</i>	μ_v 0°.	μ_v 0°.	μ_v 0°.
32	50.0	13.10	14.29
64	51.49	13.56	15.60
128	52.51	14.27	17.52
256	53.40	14.63	19.39
512	54.70	15.45	21.36
1024	55.30	16.25	23.29

An examination of these data shows that the apparent minimum occurs in a 50 per cent mixture. The fluidity minimum occurs in a 40 per cent mixture. The true conductivity minimum might, however, occur at some other point.

Jones and Lindsay also made some measurements in mixtures of methyl and ethyl alcohols. No minimum was observed, the conductivities found being about what would be expected from the rule of averages. This is clearly due to the fact that, when these two solvents are brought together,

they do not exhibit the same phenomenon as is shown in the case of mixtures of the alcohols and water. We have not found any satisfactory data relative to the fluidity of mixtures of methyl and ethyl alcohols. Arrhenius¹ states that there is no striking change when the two are brought together.

The best method of comparing the variation in conductivity and in fluidity is not by a discussion of the conductivity and fluidity curves; it is better to compare the respective ratios of decrease (by per cent) of the two—that is, the differences in per cent from what would be expected from the rule of averages. These average values may be found graphically as follows: At the extremities of a straight line of chosen length, erect perpendiculars proportional in length to the respective conductivities (or fluidities) of the two components of the mixtures, and connect these by a straight line. Divide the base line into parts proportional to the composition of the various mixtures. The perpendiculars joining these points of division and the line previously drawn will be proportional in length to the various average conductivities (or fluidities). This can best be done by the use of coordinate paper. The foregoing method has been used in making the following comparisons:

Table LIX.—Variation ($\Delta\mu_v$) in Conductivity (Percentage Fall in Conductivity) of Potassium Iodide in Mixtures of Ethyl Alcohol and Water at 18°.²

	20 Per cent.	40 Per cent.	60 Per cent.	80 Per cent. C ₂ H ₅ OH by volume.
<i>v.</i>	$\Delta\mu_v$.	$\Delta\mu_v$.	$\Delta\mu_v$.	$\Delta\mu_v$.
128	0.329	0.465	0.443	0.308
256	0.334	0.472	0.450	0.311
512	0.340	0.481	0.463	0.334
1024	0.339	0.483	0.464	0.344
2048	0.340	0.482	0.464	0.343
Variation in fluidity $\Delta\phi$	0.461	0.627	0.601	0.466

It is seen that the variation in fluidity is in all cases greater than the variation in conductivity. The two variations must

¹ Ztschr. phys. Chem., I, 287 (1887).

² The conductivity data are taken from the work of Cohen (*loc. cit.*).

be compared in order to see where the effect of variation of fluidity is greatest. If the two effects were exactly equal, $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$ would equal zero. In this relation we have a means of comparing the two effects. We have made the comparison in the following table:

Table LX.—Comparison of Variations in Conductivity and in Fluidity.

<i>v.</i>	20 Per cent.	40 Per cent.	60 Per cent.	80 Per cent $\text{C}_2\text{H}_5\text{OH}$.
	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$
	$\Delta\phi$	$\Delta\phi$	$\Delta\phi$	$\Delta\phi$
128	0.287	0.258	0.263	0.339
256	0.282	0.247	0.258	0.333
512	0.239	0.231	0.232	0.283
1024	0.239	0.231	0.232	0.262
2048	0.239	0.231	0.232	0.262

It is evident that the effect of variation of fluidity on conductivity is greatest in the 40 per cent mixture, for here the values of the quotients are least. It is seen that the effect increases with increasing dilution, and finally becomes constant.

Similar comparisons are given for potassium iodide in mixtures of methyl alcohol and water at 0° and at 25° , using Jones and Lindsay's results.

Table LXI.—Variation (Percentage Fall) in Conductivity of Potassium Iodide in Mixtures of Methyl Alcohol and Water at 25° and at 0° .

<i>v.</i>	20 Per cent.	40 Per cent.	50 Per cent.	65 Per cent.	80 Per cent CH_3OH .
	$\Delta\mu_v$.	$\Delta\mu_v$.	$\Delta\mu_v$.	$\Delta\mu_v$.	$\Delta\mu_v$.
64 $—0^\circ$		0.479	0.494	0.456	
25°	0.237	0.356	0.372	0.350	0.267
128 $—0^\circ$	0.361	0.507	0.510	0.478	
25°	0.257	0.368	0.386	0.360	0.283
256 $—0^\circ$	0.365	0.509	0.502	0.486	
25°	0.262	0.377	0.394	0.371	0.300
512 $—0^\circ$	0.366	0.510	0.513	0.489	
25°	0.262	0.379	0.399	0.381	0.313
1024 $—0^\circ$	0.361	0.503	0.508	0.490	
25°	0.262	0.379	0.402	0.386	0.320
0°	0.543	0.695	0.695	0.682	
25°		0.575			

Table LXII.—Comparison of Variation in Fluidity and in Conductivity, $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$.

v .	20 Per cent.	40 Per cent.	50 Per cent.	65 Per cent.	80 Per cent CH ₃ OH.
	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$
64 —0°		0.311	0.289	0.331	
25°	0.354	0.309	0.304	0.329	0.385
128 —0°	0.335	0.275	0.266	0.299	
25°	0.300	0.285	0.276	0.321	0.346
256 —0°	0.325	0.268	0.261	0.300	0.309
512 —0°	0.326	0.266	0.262	0.282	
25°	0.289	0.264	0.251	0.281	0.279
1024 —0°	0.335	0.276	0.270	0.282	
25°	0.286	0.264	0.246	0.272	0.262

In the following table comparison is made for lithium nitrate :

Table LXIII.—Variation (Percentage Fall) in Conductivity of Lithium Nitrate in Mixtures of Methyl Alcohol and Water at 0° and 25°. (From Jones and Lindsay's Data.)

v .	25 Per cent.	50 Per cent.	75 Per cent CH ₃ OH.
	$\Delta\mu_v$.	$\Delta\mu_v$.	$\Delta\mu_v$.
32 —0°	0.406	0.508	0.432
25°	0.285	0.384	0.333
64 —0°	0.417	0.518	0.443
25°	0.296	0.392	0.345
128 —0°	0.432	0.532	0.466
25°	0.307	0.403	0.358
256 —0°	0.436	0.535	0.472
25°	0.314	0.406	0.362
512 —0°	0.441	0.541	0.477
25°	0.310	0.408	0.354
1024 —0°	0.434	0.541	0.477
25°	0.300	0.411	0.354
—0°	0.600	0.695	0.661
25°	0.456	0.575	0.481

Table LXIV.—Comparison of Variation in Conductivity and in Fluidity, $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$, at 0° and at 25°.

<i>v.</i>	25 Per cent.	50 Per cent.	75 Per cent CH ₃ OH.
	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$
32 —0°	0.323	0.269	0.345
25°	0.375	0.332	0.308
64 —0°	0.305	0.255	0.330
25°	0.351	0.318	0.283
128 —0°	0.280	0.235	0.294
25°	0.327	0.300	(0.255)
256 —0°	0.273	0.230	0.284
25°	0.311	0.294	(0.247)
512 —0°	0.265	0.222	0.277
25°	0.318	0.290	0.264
1024 —0°	0.277	0.222	0.277
25°	(0.344)	0.285	0.264

In the following tables are given the data for sodium iodide, using my own results :

Table LXV.—Variation (Percentage Fall) in Conductivity of Sodium Iodide in Mixtures of Methyl Alcohol and Water at 0° and at 25°.

<i>v.</i>	25 Per cent.	50 Per cent.	75 Per cent CH ₃ OH
	$\Delta\mu_v$.	$\Delta\mu_v$.	$\Delta\mu_v$.
32 —0°	0.400	0.485	0.411
25°	0.277	0.357	0.298
64 —0°	0.406	0.505	0.419
25°	0.283	0.378	0.310
128 —0°	0.409	0.515	0.423
25°	0.297	0.395	0.318
256 —0°	0.408	0.508	0.433
25°	0.313	0.395	0.330
512 —0°	0.409	0.500	0.446
25°	0.321	0.402	0.333

Table LXVI.—Comparison of Variations in Fluidity and Conductivity.

<i>v.</i>		25 Per cent.	50 Per cent.	75 Per cent CH ₃ OH.
		$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$	$\frac{\Delta\phi - \Delta\mu_v}{\phi\Delta}$	$\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$
32	—0°	0.333	0.302	0.378
	25°	0.392	0.379	0.384
64	—0°	0.323	0.273	0.366
	25°	0.379	0.343	0.355
128	—0°	0.320	0.260	0.360
	25°	0.348	0.318	0.339
256	—0°	0.320	0.269	0.345
	25°	0.313	0.313	0.314
512	—0°	0.320	0.281	0.325
	25°	0.296	0.301	0.308

Finally we give a comparison of the temperature coefficients of conductivity for various electrolytes and the temperature coefficients of fluidity for the various mixtures.

The volumes were 1024 for KI, LiNO₃, SrI₂; 256 for NaI; 128 for CdI₂ 256 for Ca(NO₃)₂.

The temperature coefficients for the ethyl alcohol mixtures are seen to be most nearly equal in the 65 per cent mixture for potassium iodide; for the other salts in the 50 per cent mixture.

Table LXVII.—Comparison of Temperature Coefficients of Conductivity and Fluidity for Various Electrolytes in Ethyl Alcohol-Water Mixtures.

	0 Per cent.	50 Per cent.		100 Per cent CH ₃ OH.	
φ —0°	55.39	14.15		55.5	
φ —25°	112.00	41.77		85.88	
$\frac{1}{\varphi_{25}} \cdot \frac{\Delta\varphi}{\Delta t}$	0.0249	0.0250	0.0264	0.0216	0.0142
$\frac{1}{\mu_{25}} \cdot \frac{\Delta\mu}{\Delta t}$					
KI	0.0172		0.0237		0.0135
<i>v</i> = 1024					
LiNO ₃	0.0184		0.0251		0.0138
<i>v</i> = 1024					
SrI ₂	0.0272		0.0247		0.0199
<i>v</i> = 1024					
Ca(NO ₃) ₂	0.0182	0.0233	0.0245	0.0210	0.0131

Table LXVIII.—Comparison of Temperature Coefficients of Conductivity and of Fluidity for Various Electrolytes in Methyl Alcohol-Water Mixtures.

	25 Per cent.	40 Per cent.	50 Per cent.	65 Per cent.	75 Per cent.	100 Per cent CH ₃ OH.
φ —0°	30.6	27.0	27.8	34.5	39.75	131.3 —3°.8
φ —25°	69.04	63.4	60.65	68.9	81.83	182.1 —25°.4
$\frac{1}{\varphi_{25}} \cdot \frac{\Delta \varphi}{\Delta t}$	0.0223	0.0230	0.0216	0.0200	0.0205	0.0123
$\frac{1}{\mu_{25}} \cdot \frac{\Delta \mu_v}{\Delta t}$						
KI		0.0205	0.0197	0.0187		0.0121
NaI	0.0202		0.0202		0.0179	0.0117
LiNO ₃	0.0211		0.0203		0.0182	0.0118
						$\nu = 256$
SrI ₂	0.0213		0.0210		0.0177	0.0104
CdI ₂	0.0238		0.0220		0.0178	

The temperature coefficients of the mixtures were calculated from Noack's¹ data.

It is evident from Table LXVII that for the four salts KI, LiNO₃, SrI₂, and Ca(NO₃)₂, in most mixtures, the quotient $\frac{\mu_v}{\varphi}$ is constant to within 10 per cent (5 per cent for LiNO₃). The same is true for the mixtures of methyl alcohol and water.

Discussion of Results.

The value of the quotient $\frac{\Delta\varphi - \Delta\mu_v}{\Delta\varphi}$ is a measure of the parallelism between the two phenomena, decrease in conductivity and decrease in fluidity. If the decrease were the same in both cases, other conditions being the same, the value of the quotient would be zero. The fact that it is not zero indicates that the decrease in ionic mobility resulting from the decrease in fluidity is not proportional to this latter.

When we come to compare the effect in the case of potassium iodide in mixtures of the two alcohols and water (Tables LV. and LVII.), it is seen that the effect of decrease of fluidity on ionic mobility is greatest in the ethyl alcohol mixtures, or the two effects are here most nearly parallel. The effect is less for potassium iodide in methyl alcohol mixtures at both temperatures of observation, 0° and 25°. It is to be remembered that we are leaving out of account possible differences of dissociation. Increase in dissociation (in the mixture) over that of the corresponding aqueous solution would subtract from the effect of decrease in fluidity. Apparently, this possible change in dissociation cannot be very great, as some of our measurements show—not more than 1 or 2 per cent. A far greater and entirely impossible change in dissociation would be necessary to account for the difference in the two effects.

The minimum is much more pronounced in the methyl alcohol mixtures. It occurs, however, in the ethyl alcohol mixtures generally at 0°, but is not very marked. We have just seen that the real effect is greater in the latter case, when we make

¹ *Loc. cit.*

a proper comparison. The reason why it is not so evident in the case of the ethyl alcohol mixtures, is to be found in the small conductivities in ethyl alcohol, these, in turn, as will be shown in the last part of this dissertation, being small, on account of the relatively great viscosity of ethyl alcohol, and its rather small dissociating power. On the other hand, the phenomenon does exhibit itself in the other mixtures, and this is because of the high conductivities in methyl alcohol, these being high on account of the small viscosity of methyl alcohol and its relatively great dissociating power.

Considering all of the salts in the various mixtures, it is seen that, in general, the effect of increased viscosity on conductivity is greatest in that mixture in which the minimum in conductivity occurs. In some cases the maximum effect occurs elsewhere. For example, for lithium nitrate (Table LX.) at 25° the maximum effect is in the 75 per cent mixture, while the minimum in conductivity occurs for the most part in the 50 per cent mixture.

The explanation of this is found in the fact that, although in the one mixture the effect is greater, it is offset by the effect of the smaller fluidity of the other mixture, that of the 75 per cent mixture being 81.8, and that of the 50 per cent mixture being only 68.9. In cases where the minimum shifts with increase in dilution, the probable explanation is to be found in variation in increase of dissociation accompanying further dilution.

The result of variation in the temperature is also shown in the tables—particularly in the case of the lithium salt (Table LX.). At 0° the maximum effect is in the 50 per cent mixture, at 25° in the 75 per cent mixture.

In the two tables (LXVII. and LXVIII.) is given a comparison of the temperature coefficients of fluidity and of conductivity for various electrolytes in the various mixtures of methyl alcohol and water, and also for ethyl alcohol mixtures, for which the data are more meager.

From Table LXVIII. it is evident that the temperature coefficients of conductivity and fluidity do not differ markedly,

particularly for some salts. For potassium iodide they are most nearly equal in the 65 per cent mixture, differing by only 7 per cent. For the other salts in the 50 per cent mixture the agreement is closest, and the differences are in no cases greater than for potassium iodide in the 65 per cent mixture. In some instances the agreement is seen to be much closer (SrI_2 , CdI_2).

For the ethyl alcohol mixture of 50 per cent, the temperature coefficients differ to about the same degree as in the methyl alcohol mixtures. In other words, $\frac{\mu_v}{\phi} = \text{constant}$.

These facts are significant, as will appear from the latter part of this dissertation.

The conclusion is, then, that the decrease in conductivity of electrolytes in binary mixtures of various alcohols and water, which is in some cases accompanied by the minimum conductivity observed by Zelinsky and Kratiwin, is caused primarily by a diminution in the fluidity of the solvent, and a consequent decrease in ionic mobility.

IV.

Viscosity and Conductivity.

The viscosity of a liquid or solution is defined as being the force (in dynes) necessary to move a layer of the liquid or solution 1 molecule in thickness, and of unit area (1 sq. cm.) over another layer of the liquid, with unit velocity (1 cm. per sec.). The symbol η is used for the coefficient of viscosity.

The fluidity of a liquid is the reciprocal of its viscosity $= \frac{1}{\eta}$.

That there is a connection between the viscosity of a solvent and the electrical resistance of solutions of electrolytes in the solvent, has long been known. Or, what amounts to the same thing, there is a parallelism between fluidity and conductivity.

There have been a number of investigations bearing on this

relation. The earliest is that of Wiedemann.¹ Wiedemann's method of varying the fluidity of the solution was by varying the concentration. From his study of solutions of copper sulphate of different concentrations, Wiedemann concluded that the conductivity is directly proportional to the viscosity of the solution; that is, $\frac{K\eta}{p} = \text{const.}$, where K is the conductivity, η the coefficient of viscosity, and p the concentration of the solution in parts by weight of electrolyte to 100 parts of solvent.

Grottrian,² in his investigation, used a second method of varying fluidity, that is, by varying the temperature. A comparison was made between the temperature coefficients of fluidity and of conductivity. Grottrian found that in many cases the two coefficients are approximately the same. Wiedemann and Grottrian had worked with solutions of rather high concentration. Thinking that less irregularities would be exhibited by dilute solutions, Stephan³ made a study of the conductivities of dilute solutions, containing not more than 5 per cent of sodium, potassium, and lithium chlorides, and of sodium and potassium iodides, in mixtures of ethyl alcohol and water. Stephan thus used the third possible method of varying fluidity—that of varying the solvent. Mixtures of alcohol and water were used because of certain phenomena exhibited by them. When alcohol is added to water there is a remarkable increase in viscosity over and above what would be expected from the rule of averages. Shown graphically, by plotting the composition of various mixtures as ordinates and the viscosity of the mixtures as abscissas, the viscosity curve is seen to pass through a maximum. These facts have been illustrated and more fully treated in the first part of this dissertation. Stephan also studied the effect of temperature upon the conductivities and fluidities involved, and found, as had Grottrian⁴ in other cases, that the temperature coefficients of both are approximately equal.

¹ Pogg. Ann., 99, 229 (1856).

² *Ibid.*, 157, 130 (1876).

³ Wied. Ann., 17, 673 (1883).

⁴ *Loc. cit.*

Stephan thought to establish the relations

$$k = \frac{KH}{\eta} \quad \text{and} \quad k = \frac{w}{w'} \cdot \frac{KH}{\eta},$$

the first holding for all mixtures up to the mixture with minimum fluidity, and the second from this point on. K in both formulas is the conductivity of the equivalent aqueous solution of the salt, k is its conductivity in the mixture, H and η are the viscosity coefficients for water and for the mixture respectively. In the second relation, w is the per cent of water in the mixture, and w' the per cent of water in the aqueous alcoholic mixture of minimal fluidity. Stephan's conclusion is that ionic friction is either proportional to or equal to internal friction (viscosity); that each ion carries with it neighboring molecules of the solvent, and that the ionic friction consists in friction between these and the rest of the solvent.

The agreement with these formulas was not very close, particularly in the case of the second. Why this is so can be readily seen. Stephan did not take into account one important factor in conductivity—dissociation. Certainly, with varying mixtures, there would be varying degrees of dissociation.

Grossmann¹ made use of the data furnished by Grottrian, whose determinations of viscosity were made by the method of Coulomb. By the aid of a new formula, devised by himself, Grossmann recalculated Grottrian's results, and concluded that the product of the viscosity and the conductivity of a solution is constant, and independent of the temperature. This constancy is shown by the fact that the temperature coefficients of conductivity and of viscosity (as calculated by his method) are the same to within less than 1 per cent, and in most cases to within less than one-half of 1 per cent. This he showed to be true for solutions of the chlorides of potassium, sodium, calcium, and magnesium, and of zinc sulphate. Here the great difficulty is in the method of calculation used; its validity would have to be granted, and it is questionable whether this can be done.

¹ Wied. Ann., 18, 119 (1883).

Arrhenius,¹ in the investigation already referred to, on the effect of the addition of small quantities of non-electrolytes on the conductivity of aqueous solutions, found an empirical relation between the conductivity of the solution and the viscosity of the solvent. The equation is,

$$1000 a = c + 1000 c' (A - 1),$$

where c and c' are constants for the given solvent, A is the viscosity of a 1 per cent aqueous solution of the non-electrolyte (that of water being taken as unity), and a is the coefficient a in the equation,

$$l = l_0 \left(1 + \frac{a}{2x} \right)^2,$$

the meaning of which has already been explained.

Holland² worked in the same field as did Arrhenius. He found the relations of Stephan, already cited, inapplicable to the cases studied by him, and also that of Arrhenius just given. Holland concludes that though there is a connection between conductivity and viscosity, it is unknown.

Strindberg³ merely repeated and confirmed some of the work of Arrhenius.

Völlmer,⁴ in an admirable investigation on the conductivities of various salts in methyl and ethyl alcohols, took occasion to determine the temperature coefficients of conductivity of the solutions studied, and found that these differed very little from the temperature coefficients of viscosity of the solvents, particularly for solutions in ethyl alcohol. For example, the temperature coefficient of conductivity—the mean value of $\Delta\mu_v$ for seven salts in ethyl alcohol solution—was 1.84 per cent, $\Delta\eta$ being 1.78 per cent; similarly, the mean value of $\Delta\mu_v$ for six salts in methyl alcohol solution was 1.3 per cent, $\Delta\eta$ for methyl alcohol being 1.45. In every case, at high dilutions, there was found to be a parallelism between the two temperature coefficients.

¹ Ztschr. phys. Chem., **9**, 487 (1892).

² Wied. Ann., **50**, 261 (1892).

³ Ztschr. phys. Chem., **14**, 221 (1894).

⁴ Wied. Ann., **52**, 328 (1892).

Euler,¹ extending the work of Arrhenius² on the viscosity of mixtures, finds a connection between viscosity and ionic mobility. Arrhenius had proposed the exponential formula,

$$H(xy) = A^x B^y \quad \text{or} \quad \eta_x = A^x,$$

where H is the viscosity of the mixture, A and B are characteristic constants, x the volume per cent of the first component, and y the volume per cent of the second. In the second formula, which is another way of stating the first, A is the viscosity coefficient of a normal solution of the second component in the first as solvent, x the volume per cent. Euler extends the formula to partially dissociated electrolytes in solution, giving it the form :

$$H = S^x A^x K^x,$$

assigning a part of the viscosity to each component, S being that for the undissociated portion of the electrolyte, A and K that for anion and cation, respectively, x and y the concentrations ; for normal solutions, where the dissociation factor, α , is known, the formula becomes

$$H = S^{(1-\alpha)} A^\alpha K^\alpha.$$

Assuming that ions of the same mobility have the same viscosity constant, the constants for various ions may be calculated. S may be found by determining H for two different concentrations of the same salt, of known dissociation, by the aid of Arrhenius' formula. When the viscosity coefficients for the various (univalent) ions are thus calculated, and are plotted against the corresponding ionic mobilities, the corresponding points are seen to lie on a curve which may be expressed by the equation

$$\frac{A}{((K) - 0.68)} \frac{U}{(V)} = \text{const.},$$

where A and K are the viscosity coefficients, and U and V the ionic mobilities. The ions $\overset{+}{H}$ and $\overset{-}{OH}$ do not obey this relation. This Euler explains by reference to a hypothesis proposed as to the nature of electrolytic dissociation.³

¹ Ztschr. phys. Chem., **25**, 536 (1898).

² *Ibid.*, **1**, 285 (1887).

³ Wied. Ann., **63**, 273 (1894).

Massoulier¹ studied the conductivity of copper sulphate in aqueous solutions of glycerol, and showed that, as the viscosity increases with further addition of glycerol, the resistance of the solution increases in proportion.

Kohlrausch² discusses a hypothesis advanced by himself,³ which puts into more definite form ideas that were previously, and somewhat generally, held. Kohlrausch has shown⁴ that, in the case of monovalent ions, the temperature coefficient of ionic mobility is a function of the ionic mobility itself, just as Euler showed the ionic viscosity coefficient to be a function of ionic mobility. The exceptions are the same in both cases,

$\overset{+}{\text{H}}$ and OH^- . In the article last mentioned Kohlrausch points out that, if we plot the conductivity curves of various electrolytes in a way to show the variation of conductivity with temperature, and in like manner show the variation of the fluidity of water with change in temperature, all these curves cut the zero axis at about the same point. That is, conductivity and fluidity disappear at the same point. Of course, wide extrapolation is necessary, and this fact must be taken into account. What is more significant, the conductivity curve for certain salts, notably sodium valerate, is almost identical with the fluidity curve. Further, for certain slow moving ions, the temperature coefficient of ionic mobility is almost the same as that of fluidity.

In order to explain these facts, and to avoid the tacit assumption that ionic motion is independent of motion of the solvent, Kohlrausch proposes the hypothesis that "about every ion there moves an atmosphere of the solvent, the dimensions of which are determined by the individual characteristics of the ion". * * * "The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater dimensions."

This hypothesis accounts for the facts already given: The apparent disappearance of fluidity and conductivity at the

¹ Compt. rend., **130**, 773 (1900).

² Proc. Roy. Soc., **71**, 338 (1903).

³ Sitz. Ber. Berliner Akad., 1025 (1901).

⁴ *Ibid.*, 572 (1902).

same temperature, the coincidence in certain cases of conductivity curve and fluidity curve, the equality of temperature coefficients of ionic mobility and of fluidity, and the fact that the temperature coefficient of ionic mobility is a function of the mobility itself. As stated, the conception of such ionic hydration is not new. We have seen that a similar view was advanced by Stephan, while Ciamician,¹ Nernst,² and others attempted by diffusion methods to measure the amount of this hydration in the case of certain negative ions, and came to the conclusion that it must be small. Euler³ sees in dissociation a combination of ion and solvent—that is, an ionic hydration.

The hypothesis of Kohlrausch was proposed for binary electrolytes, at high dilutions, and with water as a solvent. Its application is therefore restricted.

A more general hypothesis, applicable to a series of solvents and to various concentrations, will have to take into account the following factors: First, the viscosity (or fluidity) of the solvent; second, the amount of dissociation in the solution; third, the dissociating power of the solvent. We shall have to find a relation between the dissociating power of the solvent and some constant property of it.

There have been various hypotheses accounting for dissociating power. Nernst⁴ finds a connection between dissociating power and the dielectric constant of the solvent. The same relation had been previously pointed out by J. J. Thomson.⁵ In general, the higher the dielectric constant of a liquid, the greater is its dissociating power.

Brühl⁶ finds in a condition of unsaturation the cause of the tendency to polymerize, and of dissociating power. He holds the view that oxygen is usually quadrivalent and that water and the alcohols, for example, containing quadrivalent

¹ *Ztschr. phys. Chem.*, **6**, 403 (1890).

² *Göttingen Nachr.*, 68, 70, 86 (1900).

³ *Wied. Ann.*, **63**, 273 (1897).

⁴ *Ztschr. phys. Chem.*, **13**, 531 (1894).

⁵ *Phil. Mag.*, **36**, 320 (1894).

⁶ *Ztschr. phys. Chem.*, **18**, 514 (1895).

oxygen, are unsaturated compounds. Hence their tendency to polymerize and their power to dissociate electrolytes.

The hypothesis of Dutoit and Aston¹ has already been referred to in another connection, and has been shown to hold quantitatively, in certain cases, for water and methyl and ethyl alcohols. We have seen that, for solutions of certain salts in these solvents, the amount of dissociation (as determined from conductivity) is directly proportional to the association factor of the solvent. The hypothesis does not apply in the case of acetic acid solutions, nor does it hold for solutions in acetone.

It is plain that the hypothesis of Dutoit and Aston does not go very deeply into the phenomena; all that it asserts is that there is a parallelism between the amount of dissociation effected by the solvent, and the amount of its own association. The two may have no causal connection; the relation may arise simply from the fact that the two properties, amount of dissociation and amount of polymerization, are functions of some other property of the solvent. The Thomson-Nernst hypothesis, however, offers an explanation of more profound significance.

Dutoit and Friderich² make an attempt to find a connection between conductivity, viscosity, and association, and thus take a step in the direction of a more general hypothesis. From a study of the conductivities of solutions of different electrolytes in different solvents they came to the following conclusion:

“The values of $\mu\infty$ for a given electrolyte dissolved in different solvents, are a direct function of the degree of polymerization of the solvents, and an indirect function of the coefficient of viscosity of these solvents.” The relation was found to hold only in a general way—indeed hardly more than qualitatively.

When we come to consider the proposed relation it is difficult to see why it should exist; it is wholly empirical, and

¹ *Compt. rend.*, **125**, 540 (1897).

² *Bull. Soc. Chim.*, (3), **19**, 321 (1898).

it is not in accord with the hypothesis of Dutoit and Aston, for when complete dissociation is reached the association of the solvent is no longer an influencing factor. It is superfluous to discuss the matter further because, as stated, the relation does not hold quantitatively.

This will suffice to indicate what has thus far been done to show a connection between conductivity and viscosity. The relations hitherto brought to light are qualitative. Of far more importance is the establishment of a quantitative relationship. I shall show that such does exist, and propose the following hypothesis :

The conductivities of comparable, equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohols, other alcohols of the same series, acetone, etc.) are inversely proportional to the coefficient of viscosity of the solvent in question, and directly proportional to the association factor of the solvent. In case the hypothesis of Dutoit and Aston does not hold for the solvent in question, for "association factor of the solvent" must be substituted "amount of dissociation of the solution."

Formulated, the hypothesis is expressed by the relation

$$\frac{\mu_v \eta}{x} = \text{const.} \quad \text{or} \quad \frac{\mu_v \eta}{a} = \text{const.},$$

where the symbols have the usual significance.

This becomes, when $\mu_v = \mu_\infty$,

$$\mu_v \eta = \text{const.}$$

The meaning of the term "comparable equivalent solutions" needs to be defined. In comparing aqueous solutions those of the same normality (containing equal gram-molecules of electrolyte in equal volumes) are strictly comparable. It is evident that this is not the case when, for example, we come to compare solutions of the same electrolyte in different solvents. In order to be strictly com-

parable, *the solutions must contain the same number of gram-molecules of electrolyte dissolved in the same number of gram-molecules of the different solvents*, or equal weights of the (same) electrolyte dissolved in volumes of the solvents, which are proportional to the molecular volumes of the solvents in question. It is obvious that this is the only proper basis of comparison.

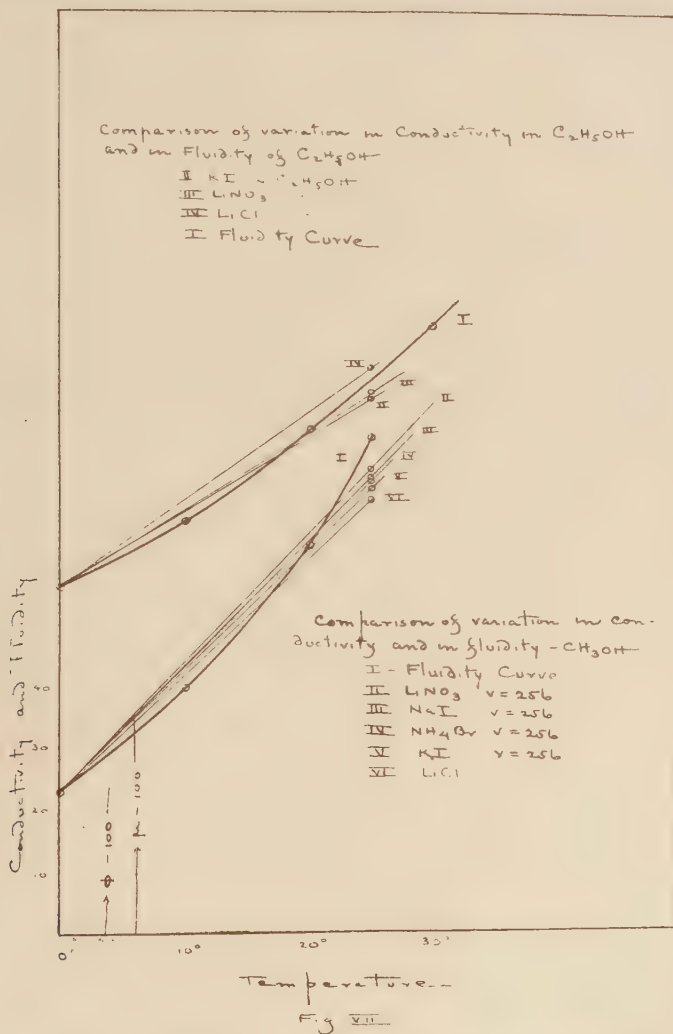
To illustrate, comparable solutions in water and in methyl alcohol would be those containing the same weight of electrolyte dissolved in 18 volumes of water and 40 volumes of methyl alcohol, because the molecular volume of water is 18, and that of methyl alcohol approximately 40. The volumes compared should always be in the ratio 18 (of water) to 40 (of methyl alcohol). Similarly, in the case of methyl and ethyl alcohols, the volumes would be as 40 to 57.5.

In the first place I have plotted (Fig. VII.) the variation in the fluidity of methyl and ethyl alcohols with temperature, making the different fluidities ordinates, and the different temperatures abscissas. Plotted with these, for the sake of comparison, are the conductivities of various binary electrolytes in solution in the two solvents. Since only two observations were made, one at 0° and the other at 25° , the variation in conductivity is shown by a straight line. If observations at intermediate points could be obtained the line would probably be curved. The first ordinate—that at 0° —is made the same in both cases. The second in the case of the conductivities is then found from the observed value by multiplication by a factor.

From an inspection of the figure (Fig. VII.) it is evident that the lines representing variation of conductivity and variation of fluidity with temperature are almost coincident. That is, the temperature coefficients are almost the same in both, the difference never being over 8 per cent, and in most cases much less than this, particularly for solutions in ethyl alcohol. Völlmer¹ has already called attention to this fact. This amounts, then, to a proof of the Kohlrausch

¹ *Loc. cit.*

hypothesis for solutions in methyl and ethyl alcohols, and such proof is necessary to establish the validity of the one proposed



It has already been shown that this is also true for certain electrolytes in certain mixtures of solvents. Though the temperature coefficients of fluidity and conductivity are the

same, the value of the quotient $\frac{\mu_v \eta}{a}$ is much greater for an electrolyte in the mixture than for the same electrolyte in the pure alcohol. It is difficult to see why this is the case—unless it be that in the mixture we have a complex solvent not to be compared with the simple one. Certainly the presence of compounds in the mixture would complicate matters. This interesting point needs further investigation.

Knowing the values of the constant for the pure solvent, and assuming the validity of the relation for the mixture, we might calculate the ionic friction. This would not be the same as the coefficient of viscosity of the mixture, but its variation with temperature would be identical with that of conductivity.

The next step is the discussion of certain data as to conductivities in the two solvents,—proof that the expression $\frac{\mu_v \eta}{x}$ holds for solutions in these solvents. The values for the coefficients of viscosity have for the most part been taken directly, or interpolated from the results of Thorpe and Rodger.¹ The values for the conductivities in the various solvents are taken from observations of Völlmer,² Carrara,² Jones and Lindsay,¹ and others, and from our own. The values for the association factors are those given by Ramsay and Shields in their first paper,³ at ordinary temperatures for methyl alcohol, 3.43, for ethyl alcohol, 2.74.

Table LXIX.— $\frac{\mu_v \eta}{x}$ for Lithium Nitrate in Methyl and Ethyl Alcohols.

Volume.	CH ₃ OH.		Volume.	C ₂ H ₅ OH.	
	0°.	25°.		0°.	25°.
128	0.1288	0.1238	191	0.1239	0.1211
256	0.1353	0.1339	381	0.1368	0.1323
512	0.1484	0.1385	763	0.1500	0.1402

The conductivities compared were for the volumes 128, 256, 512 for methyl alcohol; 190.7, 381.4, 762.8 for ethyl

¹ Phil. Trans., 185, A, 397 (1894).

² Loc. cit.

³ Ztschr. phys. Chem., 12, 433 (1893).

alcohol, these being comparable dilutions. In the case of solutions in ethyl alcohol values for the conductivities were found by interpolation.

As is seen from inspection of the table, the constants for the comparable volumes are equal to within a few per cent. Further, the constant is the same at the lower and at the higher temperature. Of course, the constants are not the same for the different volumes, for here we have used the association factor as a constant in the equation; it represents dissociation. If we were to substitute per cent of dissociation for the association factor, the values for the constant would be the same in all cases.

Altogether, the agreement of theory and fact is all that could be expected, when we consider the errors involved in the determination of the quantities used. The figures for association are certainly only approximate. Conductivities are liable to an appreciable error, and different observers give values for the viscosity coefficients differing by as much as 4 or 5 per cent.

Table LXX.— $\frac{\mu_v \eta}{x}$ for Ammonium Bromide in Methyl and Ethyl

Volume.	<i>Alcohols.</i>	
	CH ₃ OH. 25°.	C ₂ H ₅ OH. 0°.
I.	0.1369	0.1293
II.	0.1441	0.1416
III.	0.1513	0.1531

The volumes of comparison are the same as those in the case of lithium nitrate (Table LXIX.).

Values for the conductivities in ethyl alcohol are taken from the work of Jones and Lindsay; those given by them for methyl alcohol solutions are not used. Those of Carrara are taken, as they agree with values given by Zelinsky and Krapivin, while those of Jones and Lindsay do not.

In all cases agreement is as close as could be expected.

Table LXXI.— $\frac{\mu_v \eta}{x}$ for Potassium Iodide in Methyl and Ethyl Alcohols.

Vol- ume.	CH ₃ OH. 25°. Jones and Lindsay.	CH ₃ OH. 25°. Carrara.	CH ₃ OH. 0°. Jones and Lindsay.	C ₂ H ₅ OH. 25°. Jones and Lindsay.	C ₂ H ₅ OH. 0°. Jones and Lindsay.	$\frac{\mu_v \eta}{\alpha}$ CH ₃ OH.	$\frac{\mu_v \eta}{\alpha}$ C ₂ H ₅ OH
I.	0.1377	0.1308	0.1417	0.1298	0.1359		
II.	0.1471	0.1408	0.1526	0.1428	0.1479	0.516	0.571
III.	0.1558	0.1466	0.1617	0.1544	0.1592	0.525	
IV.	0.1636	0.1513	0.1665	0.1698	0.176	0.539	0.571
∞						0.539	0.571

The volumes compared were 64, 128, 256, and 512 for methyl alcohol; for ethyl alcohol, 95.7, etc. Both Jones and Lindsay's¹ and Carrara's¹ values for conductivities in methyl alcohol were used in order to compare the results. In some cases those of the one give better agreement, in other cases those of the other, indicating that the differences are due to experimental errors.

It should be stated that in this case Gartenmeister's¹ values for the coefficients of viscosity were used. The calculations were made before it was decided to use those given by Thorpe and Rodger. It would hardly be profitable to recalculate, since the result is the same whichever set of values be employed. I have satisfied myself of this by numerous trials. In many cases three or four calculations were made, using the different constants given in the tables of Landolt and Boernstein.

Table LXXII.— $\frac{\mu_v \eta}{x}$ for Lithium Chloride in Methyl, Ethyl, and Propyl Alcohols.

Volume.	CH ₃ OH. 25°.	C ₂ H ₅ OH. 18°.	C ₃ H ₇ OH. 15°.
I.	0.1213	0.1256	0.1164
	0.1166	Völlmer—18°	

The volumes compared are 256, 403, 604. The values for the conductivities are taken from the work of Carrara and Völlmer, and for *n*-propyl alcohol, from Schlamp.² The agreement is satisfactory.

¹ *Loc. cit.*

² Landolt and Boernstein's Tabellen.

³ Ztschr. phys. Chem., 14, 274 (1894).

It is interesting to note that the relation holds for picric acid in solution in methyl and ethyl alcohol. Where the volumes compared are 205 and 270, respectively, $\frac{\mu_v \eta}{x}$ in the one case equals 0.0665, and in the other, 0.0641. The data for the comparison are furnished by Schall.¹

Other results may be summarized without further detail.

Table LXXIII.— $\frac{\mu_v \eta}{x}$ for Various Electrolytes in Different Solvents.

	CH ₃ OH.	C ₂ H ₅ OH.	n-C ₃ H ₇ OH.	
NaI	0.1438	0.1447		Jones and Carroll (25°) Völlmer (18°)
$v = 200, 283$				
$v = 750, 575$	0.157		0.159	Jones and Carroll (25°) Schlamp (15°) Völlmer (18°)
CH ₃ COONa	0.1156			Carrara (25°) Völlmer (18°)
$v = 832, 1200$	0.1123	0.1093		Völlmer (18°)
CH ₃ COOK	0.1279	0.1247		Völlmer (18°)
NaCl				
$v = 228, 340$	0.1457	0.1366		Carrara (25°) Völlmer (18°)

In all these instances the agreement continues to be satisfactory.

In the foregoing pages I have discussed all the material available in the literature. In all of the cases—some nine in number—fact and theory are in accord. It can, therefore, be fairly claimed that the proposed hypothesis becomes highly probable. Further investigation is, however, desirable, to see how widely it applies.

For solutions in which dissociation is complete the formulated hypothesis becomes $\mu \eta = \text{const.}$ The proof of the validity of this relation is, it seems to me, a crucial test. I give in the following table the necessary comparisons :

¹ Ztschr. phys. Chem., 14, 707 (1894).

Table LXXIV.— μ, η for Various Electrolytes in Various Solvents.

Electrolyte.	$\text{C}_2\text{H}_5\text{OH.}$ $n = 0.012385.$ 18°.	$\text{CH}_3\text{OH.}$ $n = 0.00666(18^\circ).$ $0.00552(25^\circ).$	$\text{CH}_3\text{COCH}_3.$ $n = 0.00353.$ 25°.	$n\text{-C}_3\text{H}_7\text{OH.}$ $n = 0.002554.$ 15°.
KI	0.567	0.530—18° 0.528—25°	0.541	
NaI	0.466	0.505—18° 0.496—25°	0.494	0.481
NH_4I		0.581	0.538	0.431
LiCl	0.377	0.416—18° 0.427—25°		
NaCl	0.434	0.479		

The values for acetone were taken from the work of Carrara,¹ those for ethyl alcohol from that of Völlmer,² those for methyl alcohol from that of Völlmer² and Carrara,² and those for propyl alcohol from the investigation of Schlamp.

When we consider the necessarily large experimental error involved in the determination of the limiting values for conductivity—an error which must certainly be greater than that involved in the determination of conductivities at ordinary dilutions—the agreement is as good as could be expected. Further, for lithium and sodium chlorides in ethyl alcohol, limiting values were probably not reached, for with them Völlmer did not go to a dilution as high as in other cases. The true values for these salts would probably be greater than the values given in the table, thus making a still better agreement.

IV.

Summary and Conclusions.

1. The investigations of Zelinsky and Krapivin, and of Jones and Lindsay, have been extended, and the occurrence of the minimum in conductivity has been shown for three substances, cadmium iodide, sodium iodide, and hydrochloric acid, in mixtures of methyl alcohol and water.

2. The dissociation (as determined from conductivity) of sodium and potassium iodide, and potassium bromide in 50 per cent methyl alcohol, has been determined and has been

¹ Gazz. Chim. Ital., 27 (1), 207 (1897).

² *Loc. cit.*

found to be greater than that in water at the corresponding dilution.

3. It has been shown that the explanation of the minimum in conductivity offered by Jones and Lindsay is not entirely satisfactory. The phenomenon has been shown to be dependent primarily upon the decrease in fluidity which results when the components of the solvent are mixed.

4. The hypothesis of Dutoit and Aston has been proved quantitatively for certain salts in three solvents—water, methyl alcohol, and ethyl alcohol.

5. The hypothesis of Kohlrausch (formation of an atmosphere of the solvent around the ions in solution) has been shown to hold for binary electrolytes in methyl and ethyl alcohols.

6. A hypothesis correlating conductivity, association, and viscosity (or fluidity) has been proposed, and has been shown to hold for all the cases available for discussion.

BIOGRAPHY.

The author of this dissertation, Charles Geiger Carroll, was born in Ashland, Kentucky, on October 15, 1875. His preparatory training was received in the public schools of Pueblo, Colorado, and in the Preparatory Department of the University of Denver. In 1890 he entered the Freshman class of the University of Denver, where he continued a year. The next three years were spent in teaching in the state of Texas. In the Fall of 1896 he entered the Southwestern University, at Georgetown, Texas, receiving the B. A. degree in 1896, and the M. A. degree in 1897. Since graduation he has been connected with that institution, being at present Professor of Chemistry.

In the fall of 1901 he entered the Johns Hopkins University as a graduate student in chemistry and has been in attendance during the years 1901-2 and 1903-4. His subordinate subjects were physical chemistry and physics.

